

KINETICS OF THE LIQUID PHASE  
THERMAL ISOMERIZATION  
OF ALPHA-PINENE

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## PREFACE

Preliminary to the investigation of the kinetics of the liquid phase thermal isomerization of  $\alpha$ -pinene discussed in Chapter III it was necessary first, to develop distillation columns capable of purifying the substrate and of analyzing the reaction mixtures and second, to purify and determine the physical constants of the  $\alpha$ -pinene.

The construction and operation of efficient fractionating columns for the purification and analysis of terpenes is described in Chapter I.

The physical properties of pure samples of  $\alpha$ -pinene are given in Chapter II. Since  $\beta$ -pinene occurs with  $\alpha$ -pinene in American gum turpentine(1) it seemed advisable to determine, in addition, the physical properties of pure  $\beta$ -pinene and of known mixtures of  $\alpha$ - and  $\beta$ -pinene.

## CHAPTER I. DISTILLATION COLUMNS<sup>1</sup>

Many efficient fractionating columns have been reported, most of which have been designed primarily for petroleum fractionation. Such columns are not necessarily effective in terpene fractionation. To be satisfactory for the latter the columns must perform effectively on viscous and semi-viscous liquids at pressures of 10-20 mm. They must have a low pressure drop and small operating holdup per theoretical plate and must have a high throughput so that distillations can be made in a short time in order to minimize thermal reaction. In addition, for the purposes of this laboratory, the columns must be of economical construction, readily duplicated and must operate efficiently when heated by a Nichrome-wound jacket insulated by an outer glass tube.

Several types of column construction were considered. The cost of the Stedman and Podbelniak columns made their extensive use impossible. The concentric glass tube column of Selker, Burk and Lankelma(2), although having a very low operating holdup and H.E.T.P., apparently does not have a very high capacity and seems to require a more elaborate system of column controls than was feasible. Single-turn glass helices, a loose packing, would not operate satisfactorily for terpenes under the conditions described.

<sup>1</sup>The work discussed in this chapter was done in collaboration with W. David Stallcup.

Preliminary experiments indicated that columns packed with Berl saddles, Raschig rings, or the spiral screen type of Lecky and Ewell(3) could be economically constructed and easily operated with terpene mixtures.

Operation of distillation columns. The liquid to be fractionated is placed in the distillation flask at the bottom of the column. Heat is applied to the flask and the liquid vaporizes into the column. If the column heat is maintained close to the boiling temperature of the liquid the vapor will condense and revaporize successively throughout the column. The higher the mixture rises in the column the richer it becomes in the more volatile component.

The vapors which reach the top of the column are condensed by means of a water jacketed condenser in the column head. A thermometer registers the vapor temperature. The condensed vapors may be returned to the column or collected in a receiver. This is regulated by means of an outlet stopcock. When the stopcock is completely closed, all the liquid is returned to the column and the column then operates under total reflux.

While operating under total reflux, if the column heats are properly controlled for a period of one to several hours, a given column will produce its best results. If the column performance is to approach this maximum during a fractionation of a liquid mixture the condensate must be collected from the



head so slowly that the equilibrium between the liquid and vapor in the column is disturbed as slightly as possible. The rate of collection is controlled by means of the outlet stopcock. If this rate is slow most of the liquid will be returned to the column through a calibrated drop-counter. The ratio of the volume of liquid returned to the column to the volume of liquid collected is called the reflux ratio. The higher the reflux ratio the more nearly are equilibrium conditions maintained and the greater is the operating efficiency of the column.

An industrial plate column contains a series of plates, or levels. When in operation a liquid phase is retained on the surface of each plate. The liquid is constantly vaporizing and the vapors pass through slots into the liquid layer on the plate above. For these columns, a perfect plate is defined as one in which equilibrium is maintained between the liquid and vapor phases(4).

Such a condition may be produced many times in a laboratory distillation column since the vapor condenses and re-vaporizes successively throughout the column. The height of a packed column equivalent to a perfect plate is such that the vapor at the top of the height is in equilibrium with the liquid at the bottom. This is termed the H.E.T.P. (height equivalent to a theoretical plate) and is a measure of the efficiency of the column packing, under a specified condition of operation.

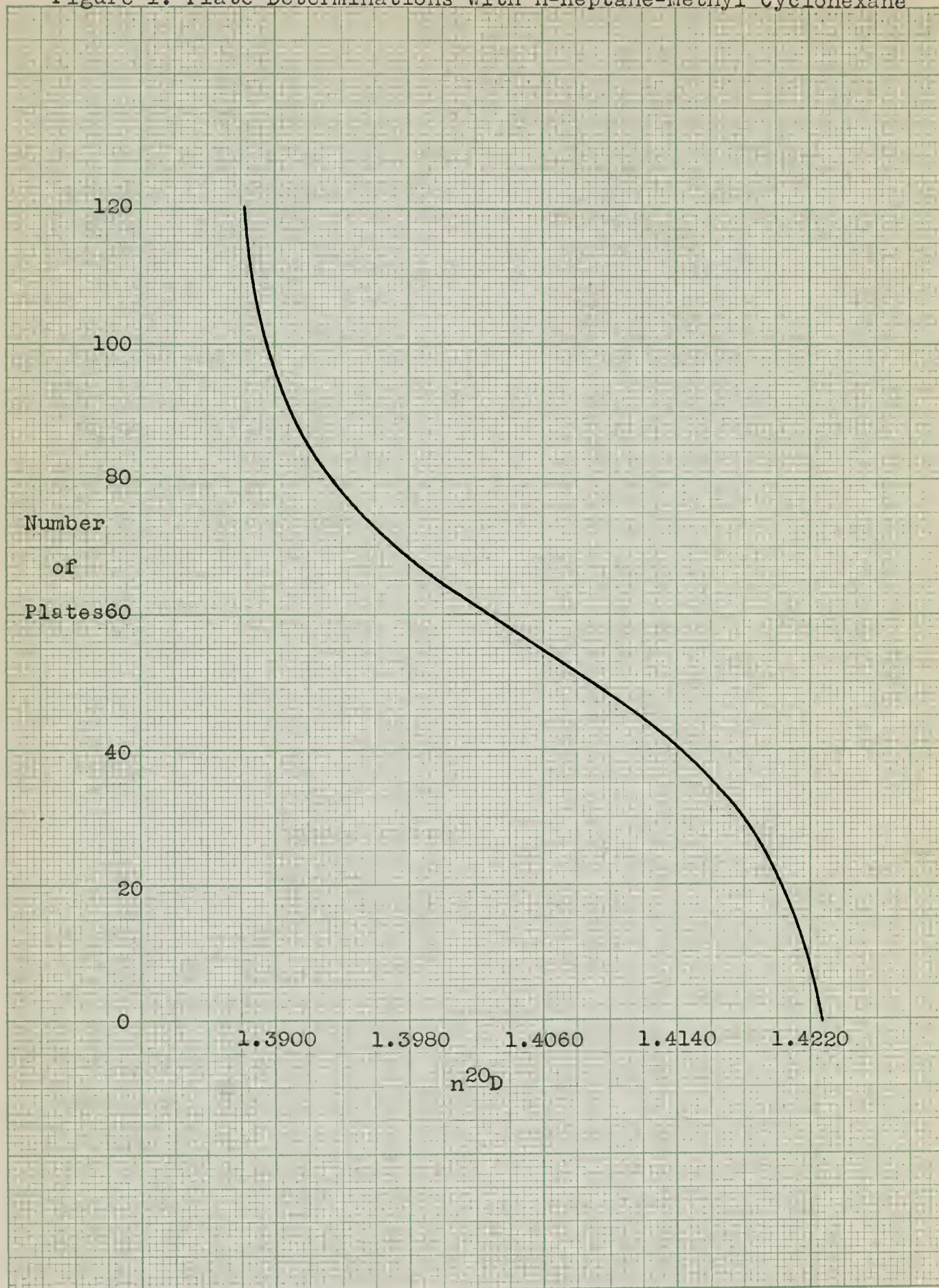
Tests and Measurements. Descriptions of the columns and test data are recorded in Table 1, page 10.

To determine the column efficiency a mixture of n-heptane and methyl chclohexane was refluxed in the column at atmospheric pressure until equilibrium had been attained. At this point two small samples were taken, one from the head and the other from the distillation flask. The refractive indices of these samples were measured and the number of plates were read directly from a graph (Figure 1), page 5-A. This graph was suggested by Lecky and Ewell(3) from the data of Beatty and Calingaert(5) and Bromiley and Quiggle(6). The relations on which it is based, and its derivation therefrom, are given by Stallcup(7a). In Table 27 (appendix) are tabulated the experimental data from which the column efficiencies were determined.

The operating holdup of the column is the volume of liquid present in the column during the distillation. This was measured by the method of Tongberg, Quiggle and Fenske(8). In this method, a weighed amount of a non-volatile compound, such as stearic acid, is dissolved in a weighed amount of a volatile compound, benzene, and the mixture is refluxed in the column under operating conditions. A sample of several grams is taken from the distilling flask and weighed. The benzene is removed from the sample on a steam bath and the sample is weighed again. These two weighings are used to calculate the relative amounts of the two compounds in the



Figure 1. Plate Determinations with n-Heptane-Methyl Cyclohexane





distillation flask from which the weight of benzene remaining in the flask may be determined. This weight subtracted from the original weight of mixture in the flask must be the weight of benzene present in the column while it is in operation. Conversion of this weight to volume gives the operating holdup of the column. The data is given in Table 28 (appendix). The large size of column 7 made the direct measurement of its operating holdup impracticable. Instead, a column 21 inches long of identical construction was tested.

1. Original concentration of stearic acid: 10.2%
2. Original weight of mixture: 67.9 g.
3. Weight stearic acid =  $0.102 \times 67.9 =$  6.9 g.
4. Final concentration of stearic acid: 16.8%
5.  $(0.168)X = 6.9$  g. where X is the weight of mixture in kettle after refluxing.
6.  $X = 6.9 / 0.168 =$  41.1 g.
7. Weight benzene in column =  $67.9 - 41.1 =$  26.8 g.
8. Volume benzene in column =  $\text{wt.} / \text{density}(0.89) = 30.1$  cc.

This corresponds to an operating holdup of 67 cc. of benzene for column 7.

The operating holdup of a column is an important factor, particularly in analytical distillations, since the column holdup should be small with respect to the volume of the mixture which is fractionated.

The non-drainable holdup was determined as recommended by Ward(9) in which a known volume of benzene was poured into the top of the column and the volume of benzene collected at the bottom of the column during the first minute was observed. The difference in these two volumes equals the non-drainable holdup.

Pressure drops were measured on columns 7 and 8 by connecting the manometer alternately to the kettle and the head by means of a double diagonal stopcock. When measured in this way the pressure drop in column 7 was 2 mm. at a head reflux of 2.5 ml. per minute, distilling B-pinene at 20 mm. Column 8, when distilling B-pinene at 20 mm. pressure with a head reflux of 0.8 ml. per minute, had a pressure drop of 2.5 mm.

#### Construction and Performance

Raschig rings (4x4 mm.) in column 1 gave an H.E.T.P. of 2.1 inches. This was a 120 cm. (4 foot) column of 11 mm. (0.43 inch) inside diameter. Because of its high operating holdup (0.5 ml./plate) this column could not be used for analysis. Peters and Baker(10) stated that unsatisfactory results were obtained when 4x4 mm. Raschig rings were used in an analytical column.

Berl saddles (4x4 mm.) in column 2 gave essentially the same H.E.T.P. (2.0 inches) as the Raschig rings in a column of the same size. However, when column 3 of 19 mm. (0.75 inch) inside diameter was filled with these Berl saddles the H.E.T.P.

decreased to 3.25 cm. (1.3 inches). This value is comparable with the best values reported for other loose packings(11) with the exception of single-turn stainless wire helices(12).

These data and previous experiments with the distillation of terpenes at 20 mm. pressure using 4x4 mm. Berl saddles indicate that this is a satisfactory type of packing for purification of components in the more readily separable terpene mixtures. For some substances Berl saddles should not be used because of the catalytic nature of their unglazed porcelain surface.

Spiral screen columns were made of two different sizes.

A. Laboratory columns for large quantities of material.  
Four foot lengths of the following columns were made.

Column 4. H.E.T.F. 4.6 inches. Stainless steel gauze (60x60 mesh) was used to make washers of outside diameter (o.d.) 37 mm. (1.50 inches) and inside diameter (i.d.) 10 mm. (0.40 inch). One-eighth inch of the outer edge of the washer was cupped at an angle of 45 degrees. A sector of approximately 20 degrees was removed from each washer and the washers were spot-welded together into a spiral group of twenty-four. By joining these groups in a similar manner, any desired length could be obtained. This spiral was then placed on the inner glass tube. A stiff wire spiral spacer, made of 1.8 inch iron wire, with five turns



to the inch was screwed into the gauze spiral. Long stiff rods were welded to the ends of the spacer to permit pulling as well as pushing of the screen into the glass tubing, the i.d. of which was about 1/16 inch less than the o.d. of the cupped spiral. At intervals during the insertion, the exposed gauze spiral was tightened on the inner tube in order to ensure a more uniform fit. When the column was assembled the spacer was removed by turning it in the proper direction.

Column 5. H.E.T.P. 2.8 inches. To make a tighter fit the diameter of the inside tube was increased. Stainless steel gauze washers (60x60 mesh), o.d. 37 mm. (1.50 inches), i.d. 18 mm. (0.71 inch), were used. The column was assembled by the same procedure as described above.

Column 6. H.E.T.P. 1.3 inches. The spiral screen packing of column 5 was removed, ground on the mandrel to the desired outside diameter and inserted in a glass tube, the inside diameter of which was about 1/8 inch smaller.

Column 7. H.E.T.P. 0.66 inch; operating holdup per plate was 0.95 ml. Stainless steel gauze washers (50x50 mesh) were used of o.d. 37 mm. (1.50 inches), i.d. 18 mm. (0.71 inch). The procedure for assembly of this column followed that for column 4. However, after spot-welding together the washers of this stiffer 50x50 mesh gauze the spiral was ground as described for column 6 and then was placed on the inner rod and inserted in a glass tube of the proper inside diameter. This column is comparable to those reported by Lecky and Ewell(3).

Table 1  
Columns and Test Data

	Column Number				
	1	2	3	7	8
Column Packing	4x4 mm. Raschig rings	4x4 mm. Berl saddles	4x4 mm. Berl saddles	50x50 mesh screen spiral	60x60 mesh screen spiral
Inside Diameter, inches	0.43	0.43	0.75	1.50	0.40
O.d., Inner Tube, inches	----	----	----	0.71	0.10
Packing Height, inches	46	48	27	46	46
Total Plates	22	24	21	70	64
H.E.T.P., inches	2.1	2.0	1.3	0.66	0.72
Operating Holdup per Plate, ml.	0.5	0.5	0.7	0.95	0.14
Nondrainable Holdup, ml.	10	8	11	28 <sup>a</sup>	5 <sup>b</sup>

<sup>a</sup>Nondrainable holdup, B-pinene, 40 ml.

<sup>b</sup>Nondrainable holdup, B-pinene, 7.5 ml.

B. Laboratory columns for small quantities of material.

Column 8. H.E.T.P. 0.72 inch; operating holdup per plate was 0.14 ml. The procedure in making this four foot length of column was the same as that described for column 4 since the grinding used in columns 6 and 7 was not necessary for columns of small diameter. The column was made with stainless steel gauze washers (60x60 mesh), o.d. 10 mm. (0.40 inch), i.d. 2.5 mm (0.10 inch). The washers had a 1/16 inch cup around the outer edge. Nickel wire was used as the inner rod and the spacer used had seven turns to the inch.

Operation of spiral screen columns with terpenes. The columns were thoroughly wetted down with the liquid and the column temperature was adjusted to within 2° of the boiling point of the more volatile component. The columns were operated at total reflux until liquid-vapor equilibrium was attained, at which time continuous fractionation was begun.

Column 7. Table 29 (appendix) contains the refractive index data illustrating how this column functioned at 20 mm. pressure on the separation of  $\alpha$ -pinene from the B-pinene in a commercial sample of  $\alpha$ -pinene obtained from gum turpentine. The column was operated with a head reflux of 2.5 ml. per minute as measured by a calibrated drop counter. No attempt was made to measure reflux at the bottom of the column. A head reflux ratio of 25 to 1 was used. This column had also



been used successfully to obtain pure B-pinene from commercial material.

Table 30 (appendix) gives the refractive index data of a separation of a prepared mixture of a-pinene, camphene, and B-pinene at 20 mm. by a 180 cm. (6 foot) length of a column of the diameter and construction of column 7. A head reflux ratio of 40 to 1 used during the collection of pure a-pinene was purposely maintained throughout the transition from a-pinene to camphene. This readily explains the gradual shift toward camphene at the beginning of the transition and the holdup of approximately 110 ml. In the transition from camphene to B-pinene the head reflux ratio was increased to 60 to 1, causing a holdup of about 85 ml. which was 15 ml. less than the operating holdup of the column. Over 100 ml. of the camphene obtained had a solidifying range of 44-45°C. and the remainder solidified at temperatures not lower than 25° C. This distillation of about 800 ml. of mixture was completed in 9 days. This indicates how this column might be used for rapid analysis of large quantities.

Column 8. As a preliminary test this column was used to separate a mixture of 35 ml. of carbon tetrachloride and 35 ml. of cyclohexane into approximately 90 mole percent carbon tetrachloride and 100 mole percent cyclohexane. The holdup of the column under the conditions of operation was 13 ml. and the separation required 36 hours. The boiling point and refractive index data is given in Table 31 (appendix).

When fractionating terpenes, column 8 was so regulated that the head reflux was about 0.8 ml. per minute. A head reflux ratio of 25 to 1 was used on the plateaus of the distillation curves(7b) but usually a higher ratio of about 40 to 1 was used when passing between plateaus. The low pressure drop of this column combined with its high capacity minimizes any thermal reaction by allowing an analysis to be completed in a short period of time.

32 ml. were collected from a mixture of  $\alpha$ -pinene and B-pinene distilled through column 8 at 20 mm. pressure. These compounds boil 7.5 degrees apart at 20 mm. The data is given in Table 32. 16 ml. of  $\alpha$ -pinene, 11 ml. of B-pinene and 5 ml. of mixture boiling between the two pure components were obtained.

Table 33 (appendix) gives data for the separation of a mixture of  $\alpha$ -pinene and a dipentene cut of commercial material. The two major fractions were, respectively,  $\alpha$ -pinene and dipentene. The small middle fraction on analysis was found to be p-menthane, which the temperature plot fails to detect.

The data for the separation of a mixture of terpene alcohols at 20 mm. pressure is given in Table 34 (appendix). Prior to distillation the mixture had a relative viscosity of 31. The operation of the column for a material of this

viscosity is nearly as easy as it is for a mixture of  $\alpha$ - and B-pinene. This ease of operation with such viscous materials makes the spiral screen type of column particularly valuable in the analysis of many terpene mixtures.

#### Costs of spiral screen columns

The entire cost of column 7, including all jackets and glass standard taper joints was \$37.00; of column 8, \$35.00. Labor costs including overhead were calculated at the rate of \$1.50 per hour. Two work-hours per foot on column 7 and four work-hours per foot on column 8 were required. These costs do not include the construction of the punches for cutting the spirals which requires about 15 hours each.

#### Summary

The details of the construction of the spiral screen type of column are given.

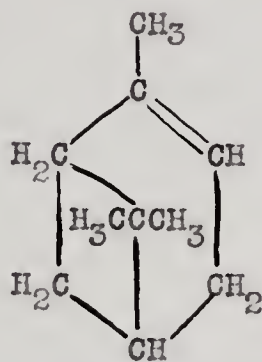
Test data for 4x4 mm. Raschig rings, 4x4 mm. Berl saddles, and the spiral screen columns are given. For a loose packing the 4x4 mm. Berl saddles have a high efficiency and are suitable for terpene fractionations.

Results are given for the operation of columns with the spiral screen packing on various terpene mixtures.

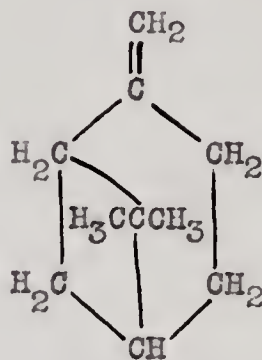


## CHAPTER II. PHYSICAL PROPERTIES OF $\alpha$ - AND $\beta$ -PINENE<sup>1</sup>

Data in the literature show a wide variation in the values for the physical constants for  $\alpha$ -pinene(I) and  $\beta$ -Pinene(II).



$\alpha$ -pinene  
(I)



$\beta$ -pinene  
(II)

With the fractionation columns previously discussed it is possible to obtain  $\alpha$ - and  $\beta$ -pinenes which should be of a higher degree of purity than has been reported heretofore.

### Preparation of $\alpha$ -pinene and $\beta$ -pinene

$\alpha$ -Pinene was prepared by the careful fractionation of four liters of commercial  $\alpha$ -pinene<sup>2</sup>, from gum turpentine, through a spiral screen column at 20 mm. pressure and a reflux ratio of 40 to 1. This column exerted 75 plates upon a mixture of n-heptane-methylcyclohexane at total reflux and atmospheric pressure. Fractions were collected at 75 cc. intervals. All

<sup>1</sup>The work discussed in this chapter was done in collaboration with W. David Stallcup.

<sup>2</sup>Furnished through the courtesy of Southern Pine Chemical Company, Jacksonville, Florida.

fractions with a refractive index in the range 1.4631-1.4633 at 25.0° were combined and refractionated through the same column. Fractions were then collected at 50 cc. intervals and their refractive indices and optical rotations were measured at 25.0°. The fractions which had constant values of refractive index and optical rotation were combined and were considered to be pure  $\alpha$ -pinene. In verification, a 100 cc. portion of the latter was fractionated through a column which had 60 plates determined as above. No change in those two physical constants was noted at any point during collection of the distillate.

$\alpha$ -pinene from wood turpentine<sup>1</sup> was desired also. The preparation of this pure component from wood turpentine involves its separation from a small amount of camphene which boils about 3° higher. The intermediate fractions having constant refractive indices and optical rotations at 25.0° were then combined and refractionated. The material thus obtained had constant physical properties and was of the same purity as the  $\alpha$ -pinene from gum turpentine.

The B-pinene used was prepared in an analogous manner from commercial B-pinene<sup>2</sup> obtained from gum turpentine.

<sup>1</sup>Purchased from Hercules Powder Company.

<sup>2</sup>Furnished through the courtesy of Southern Pine Chemical Company, Jacksonville, Florida.

These purified pinenes had the following constants:

	B.p., °C. (20.0 mm.)	$n_{25.0}^D$	$d_{25.0}^{25.04}$	$(a)_{25.0}^D$
a- (gum)	52.2	1.4631	0.8542	- 3.83
a- (wood)	52.2	1.4631	0.8542	+34.07
B- (gum)	59.7	1.4768	0.8666	-21.49

These constants are in close agreement with unpublished data of Bain(13), with much of the data of Falkin and co-workers(1,14), with data of Waterman, Van't Spijker and Van Westen(15) and with some of the data of Dupont(16).

#### Experimental

Density Measurements. These were made with a 25 ml. density bottle. In all cases values were obtained at least in duplicate which checked to the fourth decimal place. The thermostat was controlled by means of an Aminco Metastatic Thermoregulator connected to a vacuum tube relay circuit developed by Hershberg and Huntress(17). The thermoregulator controlled the temperature within a limit of  $\pm 0.02^\circ$ .

Mixtures of a- and B-pinene were made up to known concentrations by weight. Measurements of the variation of density with concentration were made using a-pinene from both gum and wood turpentine. The densities of the mixtures were independent of the source of the a-pinene used. The average deviation of the density determinations was 0.00004. These data are given in Table 2, page 18, and may be expressed at  $25.0^\circ$  by the



Table 2  
Densities of Mixtures of  $\alpha$ - and B-pinene

Mole Fraction B-pinene	$d_4^{25.0}$ observed	$d_4^{25.0}$ calculated
0.000	0.8542	0.8542
0.162	0.8562	0.8563
0.292	0.8579	0.8579
0.402	0.8593	0.8593
0.497	0.8605	0.8605
0.623	0.8621	0.8621
0.703	0.8630	0.8630
0.846	0.8647	0.8648
1.000	0.8666	0.8666

equation

$$d_4^{25} = 0.8542 + 0.0129X - 0.0005X^2 \quad (1)$$

in which X is the mole fraction of B-pinene.

Refractive Index Measurements. These were obtained with the pure substances and their mixtures by means of an Abbe' refractometer calibrated against a known glass. Constant temperature was maintained by circulating water through the refractometer from the thermostat described above. The average deviation of the determinations was 0.00006.

Refractive index measurements of the two pure substances for the temperature range 15-35° show that both a- and B-pinene have a coefficient of 0.00045 unit per degree. The data is recorded in Table 3, page 20.

The variation of the refractive index with concentration for mixtures of B-pinene and either gum or wood a-pinene at 25.0° may be expressed by the equation

$$n_{D}^{25.0} = 1.4631 + 0.0144X - 0.0007X^2 \quad (2)$$

where X is the mole fraction of B-pinene. The data is in Table 4, page 21.

The molar refractions of the pure components were calculated using the standard atomic refraction values of Auwers and Eisenlohr and also a value of 0.48 for the cyclobutane ring. In this manner the value of 43.99 was obtained for

Table 3

## Variation of Refractive Index with Temperature

t°C.	$\alpha$ -pinene $n_D$	$\beta$ -pinene $n_D$
13.7	1.4682	1.4818
17.9	1.4663	1.4800
20.1	1.4653	1.4789
24.0	1.4636	1.4772
27.3	1.4621	1.4758
30.4	1.4607	1.4743
34.5	1.4588	1.4725
25.1	1.4631	1.4768



Table 4  
Refractive Indices of Mixtures of  $\alpha$ - and B-pinene

Mole Fraction B-pinene	$n^{25.0}_{\text{D}}$ observed	$n^{25.0}_{\text{D}}$ calculated
0.000	1.4631	1.4631
0.095	1.4645	1.4645
0.203	1.4660	1.4660
0.300	1.4673	1.4674
0.400	1.4687	1.4687
0.493	1.4700	1.4700
0.588	1.4713	1.4713
0.694	1.4727	1.4727
0.781	1.4739	1.4739
0.902	1.4755	1.4755
1.000	1.4768	1.4768

both a- and B-pinene. From the observed data the values of 43.93 and 44.40 were calculated for a- and B-pinene, respectively, by use of the Lorenz-Lorentz equation:

$$Mr_D = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2} \quad (3)$$

where  $Mr_D$  is the molecular refraction

$M$  is the molecular weight of the compound

$d$  is the density of the compound

$n$  is the refractive index of the compound  
the  $Na_D$  line.

The exaltation of 0.41 for B-pinene is probably due to the presence of the exocyclic double bond. Auwers(18) has proposed that values of from 0.32 to 0.52 be added to correct for the exocyclic double bond.

Polarimetric Measurements. Since a-pinene has a rotation that varies with its source, sample, and time of year collected from the tree, the value of this constant has no diagnostic significance(19). It has been pointed out by Darmois(20) that B-pinene has a constant specific rotation regardless of its source, and that this value is  $-22.44^\circ$  for the j-line of mercury. Dupont(16) reported a value of  $-22.48^\circ$ .

All rotations were observed at  $25.0^\circ$  in a jacketed two-decimeter tube. A Duboscq polarimeter, reading by vernier to  $0.01^\circ$  of arc and equipped with suitable filters, depending on the wave length of light, was used. Readings on the same tube

could be made with an average deviation of  $0.02^{\circ}$  using the sodium light and  $0.03^{\circ}$  using a less intense mercury arc.

Listed in Table 5, page 24, are rotations of a- and B-pinene and their mixtures for the  $\text{Na}_D$  (589 mm.),  $\text{Hg}_j$  (578 mm.) and  $\text{Hg}_v$  (546 mm.) lines. Also given are the observed rotatory dispersions. The rotatory dispersion of an optically active compound is the ratio of its rotation for two different wave lengths. This value of the dispersion varies with the wave lengths used. Biot's law for the linearity of specific rotations of mixtures does not hold exactly. The maximum deviation is about  $0.3^{\circ}$  at a mole fraction of 0.5. The data could be expressed by a second degree equation. However, this relation would change with the variation in the value of the rotation of the pure a-pinene used.

Also, listed in column 3, Table 5A, are the mole fractions of B-pinene calculated by Biot's law from the observed data using the  $\text{Na}_D$  line. The deviations for the  $\text{Hg}_j$  and  $\text{Hg}_v$  lines are about the same.

Biot's law may be applied, to express rotatory dispersion for a given mixture, in the form

$$\frac{(a)_v}{(a)_D} = \frac{n_B - (a_B)_v}{n_B - (a_B)_D} + \frac{(1 - n_B) - (a_a)_v}{(1 - n_B) - (a_a)_D} \quad (4)$$

in which  $n_B$  is the mole fraction of B-pinene in the mixture,  $(a_B)_v$  and  $(a_B)_D$  are the specific rotations of B-pinene with the v-line and D-line, respectively, and  $(a_a)_v$  and  $(a_a)_D$  are



Table 5

A. Specific Rotations of Mixtures of  $\alpha$ - and B-pinene

Mole Fraction B-pinene	$(\alpha)^{25.0}_D$	Mole Fraction B-pinene Biot	$(\alpha)^{25.0}_J$	$(\alpha)^{25.0}_V$
0.000	- 3.83	-----	- 4.03	- 4.57
0.110	- 5.69	0.105	- 5.96	- 6.59
0.205	- 7.32	0.198	- 7.61	- 8.29
0.290	- 8.71	0.276	- 9.02	- 9.77
0.394	-10.53	0.379	-10.85	-11.67
0.495	-12.26	0.477	-12.61	-13.53
0.581	-13.84	0.567	-14.19	-15.17
0.680	-15.67	0.671	-16.05	-17.13
0.806	-17.90	0.796	-18.32	-19.50
0.887	-19.44	0.884	-19.86	-21.09
1.000	-21.49	-----	-21.98	-23.28

B. Dispersions of Mixtures of  $\alpha$ - and B-pinene

Mole Fraction B-pinene	$(\alpha)_V/(\alpha)_D$	Dev. $\times 10^3$	$(\alpha)_V/(\alpha)_J$
0.000	1.193	----	1.134
0.110	1.158	-9	1.106
0.205	1.132	-4	1.091
0.290	1.121	-4	1.084
0.394	1.107	0	1.076
0.495	1.103	-2	1.074
0.581	1.097	-1	1.070
0.680	1.093	-1	1.067
0.806	1.089	-1	1.064
0.887	1.085	0	1.062
1.000	1.083	----	1.059

the specific rotations of  $\alpha$ -pinene with the v-line and D-line, respectively. When the values of dispersion are calculated on this basis only slight variations from the observed dispersions are noted. This deviation is illustrated for the  $(\alpha)_V/(\alpha)_D$  dispersion by the data in column 3, Table 5B.

Dupont(20) observed that for high  $\alpha$ -pinene content (approximately 70 mole per cent or greater) the dispersion is a good indication of the  $\alpha$ -pinene content. Ordinarily the  $(\alpha)_V/(\alpha)_J$  ratio is used, probably because the two lines are obtained from the same source. However, the data show that  $(\alpha)_V/(\alpha)_D$  gives a wider dispersion range and therefore should be a more satisfactory indication of the  $\alpha$ -pinene content.

Vapor Pressure Measurements. These were determined in the pressure range from 15 to 80 mm. by use of a distillation column in which the vapors were allowed to come to equilibrium with the liquid. The column temperature was adjusted to within  $1.5^\circ$  of the temperature recorded by the condensing vapors in the head. The temperatures of the vapors were measured by the use of a calibrated mercury thermometer that could be read to  $\pm 0.05^\circ$ . The bulb of the thermometer was wrapped with a single layer of cotton gauze.

The pressure was regulated by a manostat of the Hershberg-Huntress type(17). The action of the vacuum pump on the manostat was partially checked by placing a stopcock between the pump and the manostat. The pressure fluctuations were mini-

mized by including a five gallon bottle in the system between the manostat and the column.

The manometer was connected to the head of the column so that the pressure of the condensing vapors would be recorded. The vapor pressures were measured with a Germann barometer,<sup>1</sup> using a cathetometer which could be read to 0.01 mm. The observed pressure readings were corrected to 0° for the difference in the expansion of the mercury and the brass scale at different temperatures(21) and were corrected to 45° latitude and sea level(22). At each recorded temperature about 2 cc. of liquid was collected at a reflux ratio of 20 to 1.

Equations were obtained by applying the method of averages to the corrected data. It was found that the equation

$$\log p = 8.1020 - 2213/T \quad (5)$$

represents the data for  $\alpha$ -pinene for the stated pressure range. The experimentally determined values agree with the values calculated by the empirical equation with an average deviation of 0.08 mm. and a maximum deviation of 0.2 mm. Similarly, the equation

$$\log p = 8.1504 - 2280/T \quad (6)$$

represents the data of  $\beta$ -pinene for the same pressure range. The experimentally determined values agree with the values calculated by the empirical equation with an average deviation

<sup>1</sup>Built by G.T. Armstrong.



of 0.11 mm. and a maximum deviation of 0.4 mm. The observed data and the calculations illustrating the application of the method of averages are given in Table 6, page 28, and Table 7, page 29, respectively.

The Clausius-Clapeyron equation may be written

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \quad (7)$$

where  $L$  is the latent heat of vaporization

$R$  is the molar gas constant (1.98 cal.)

$T$  is Absolute temperature

$p$  is pressure.

Assuming  $L$  and  $R$  to be constant, integration of equation (7) gives

$$2.303(\log p) = -L/RT + C$$

$$\text{and } \log p = C' - L/(2.303RT). \quad (8)$$

The general form of this equation, corresponding to equations (5) and (6) is

$$\log p = A - B(1/T)$$

$$\text{where } B = L/(2.303R)$$

$$\text{and } L = (2.303) (R) (B).$$

Thus from equations (5) and (6), the latent heat of vaporization for the stated pressure range may be shown to be 10,130 cal./mole or 74.35 cal./g for  $\alpha$ -pinene and 10,430 cal./mole or 76.60 cal./g. for B-pinene.

Table 6

Vapor Pressures of  $\alpha$ -Pinene

t°C.	T°A.	p(mm.) obs.	1/T	log p	p(mm.) calcd.	Dev.
50.2	323.4	18.1	0.003092	1.25768	18.16	+0.06
62.4	335.6	32.1	0.002980	1.50651	32.20	+0.10
66.0	339.2	37.9	0.002948	1.57864	37.84	-0.06
68.7	341.9	42.7	0.002925	1.63043	42.60	-0.10
71.9	345.1	49.0	0.002898	1.69020	48.90	-0.10
Summation (1/T) =			0.014843;	7.66346 =	Summation (log p)	

74.3	347.5	54.0	0.002878	1.73239	54.15	+0.15
76.6	349.8	59.7	0.002859	1.77597	59.65	-0.05
78.3	351.5	64.0	0.002845	1.80618	64.00	0.00
80.0	353.2	68.6	0.002831	1.83632	68.61	+0.01
82.7	355.9	76.7	0.002810	1.88480	76.56	-0.14
Summation' (1/T) =			0.014223;	9.03566 =	Summation' (log p)	

$$\begin{aligned}\text{Summation (log p)} &= \text{Summation A} - B \cdot \text{Summation (1/T)} \\ \text{Summation' (log p)} &= \text{Summation' A} - B \cdot \text{Summation' (1/T)}\end{aligned}$$

$$\begin{aligned}7.66346 &= 5A - 0.014843B \\ (-) 9.03566 &= 5A - 0.014223B \\ \hline -1.37220 &= -0.000620B\end{aligned}$$

$$B = 1.37220 / 0.000620 = 2213.$$

$$\begin{aligned}\text{Since } 5A &= 7.66346 + 0.014843B \\ 5A &= 7.66346 + 0.014843(2213)\end{aligned}$$

$$A = 8.1020$$

$$\text{Log P} = 8.1020 - 2213/T \quad (5)$$

Table 7  
Vapor Pressures of B-Pinene

t°C.	T°A.	p(mm.) obs.	1/T	log p	p(mm.) calcd.	Dev.
48.3	321.5	11.4	0.003110	1.05690	11.47	+0.07
65.7	338.9	26.5	0.002951	1.42325	26.44	-0.06
66.2	339.4	27.2	0.002946	1.43457	27.15	-0.05
70.1	343.3	32.3	0.002913	1.50920	32.27	-0.03
73.2	346.4	37.0	0.002887	1.56820	36.99	-0.01
		Summation (1/T) = 0.014807;		6.99212	= Summation(log p)	
76.1	349.3	41.9	0.002863	1.62221	41.96	+0.06
77.7	350.9	45.0	0.002850	1.65321	44.93	-0.07
81.2	354.4	52.3	0.002822	1.71850	52.04	-0.26
84.3	357.5	59.2	0.002797	1.77232	59.35	+0.15
90.6	363.8	76.0	0.002749	1.88081	76.35	+0.35
		Summation' (1/T) = 0.014081;		8.64705	= Summation'(log p)	

$$\begin{aligned}\text{Summation (log p)} &= \text{Summation A} - B \cdot \text{Summation (1/T)} \\ \text{Summation' (log p)} &= \text{Summation' A} - B \cdot \text{Summation' (1/T)}\end{aligned}$$

$$\begin{aligned}6.99212 &= 5A - 0.014807B \\ (-) \quad 8.64705 &= 5A - 0.014081B \\ \hline -1.65493 &= -0.000726B\end{aligned}$$

$$B = 1.65493 / 0.000726 = 2280$$

$$\begin{aligned}\text{Since } 5A &= 6.99212 + 0.014807B \\ 5A &= 6.99212 + 0.014807(2280)\end{aligned}$$

$$A = 8.1504$$

$$\log p = 8.1504 - 2280/T \quad (6)$$



The isobaric vapor-liquid compositions at 20.0 mm.

These were determined using a modified Sameshima apparatus(23). This is designed so that if a liquid mixture is boiled in the flask, the vapor in equilibrium with the liquid mixture is condensed in a small bulb. The overflow from the bulb, as the vaporization continues, is returned to the flask. Since the bulb has a volume of 5-6 ml., time must be allowed for complete equilibrium to be attained.

About 100 cc. of mixture was placed in the flask and then brought to equilibrium, which was generally reached within two hours but four hours were allowed before a final measurement was made. Samples were then withdrawn from the flask and from the vapor receiver. The rate of flow, which averaged 1.5 cc./min., was regulated by the voltage applied to the internal heater. The thermostat temperature was kept about 2-4° above the estimated boiling temperature of the liquid. Cold brine solution was circulated through the two condensers, each of which contained a condensing coil made from a four foot length of glass tubing. Experiments showed that there was no detectable vapor loss four hours after reaching equilibrium between liquid and vapor. The pressure control system was the same one described for the measurements of vapor pressures of the pure compounds. Samples were withdrawn by means of capillary pipets. Data were observed

by starting with mixtures rich in  $\alpha$ -pinene and going to mixtures rich in B-pinene and also by starting with mixtures rich in B-pinene and going to mixtures rich in  $\alpha$ -pinene. The compositions were determined by means of refractive index measurements and application of equation (2). The data obtained by this method are recorded in Table 8, page 32.

In order to compare the observed values with those of an ideal system, pressures,  $p_{a-}$  and  $p_{B-}$ , of the pure components were calculated by equations (5) and (6) for the temperatures listed in Table 9, page 33. Then for each temperature was calculated a liquid mixture composition at 20.0 mm. by applying Raoult's law in the form

$$20.0 = x_{a-}p_{a-} + (1 - x_{a-})p_{B-} \quad (9)$$

where  $x_{a-}$  is the mole fraction of  $\alpha$ -pinene in the liquid phase. The corresponding vapor composition was calculated from the relation

$$y_{a-} = \frac{x_{a-}p_{a-}}{20.0} \quad (10)$$

where  $y_{a-}$  is the mole fraction of  $\alpha$ -pinene in the vapor phase. The observed mole fraction of  $\alpha$ -pinene in the vapor, corresponding to liquid composition  $x_{a-}$ , in column 4, Table 9, was obtained from a plot of the vapor-liquid relations at 20.0 mm., using the data in Table 8. The difference between the observed and calculated vapor composition is a measure of the deviation from ideality of the mixtures. These deviations are listed in the last column of Table 9.

Table 8

Liquid-Vapor Composition at 20 mm.

$n_{\text{liquid}}^{25.0D}$	Mole Fraction a-Pinene in Liquid	$n_{\text{vapor}}^{25.0D}$	Mole Fraction a-Pinene in Vapor
1.4759	0.070	1.4757	0.085
1.4758	0.075	1.4756	0.090
1.4754	0.105	1.4751	0.130
1.4751	0.130	1.4747	0.160
1.4747	0.160	1.4742	0.195
1.4745	0.175	1.4740	0.215
1.4731	0.280	1.4722	0.345
1.4727	0.310	1.4718	0.375
1.4722	0.345	1.4712	0.420
1.4718	0.375	1.4708	0.450
1.4713	0.415	1.4702	0.495
1.4710	0.435	1.4699	0.515
1.4706	0.465	1.4694	0.555
1.4698	0.525	1.4686	0.610
1.4691	0.575	1.4680	0.655
1.4689	0.590	1.4678	0.670
1.4680	0.655	1.4671	0.720
1.4676	0.680	1.4667	0.745
1.4668	0.740	1.4661	0.790
1.4662	0.780	1.4656	0.825
1.4653	0.845	1.4649	0.875
1.4650	0.865	1.4647	0.890
1.4648	0.880	1.4645	0.905
1.4647	0.890	1.4644	0.910
1.4641	0.930	1.4639	0.945
1.4637	0.955	1.4636	0.965



Table 9

Deviation of Vapor Concentration as Calculated by Raoult's Law

t, °C.	$P_{a-}$ , calcd.	$P_{B-}$ , calcd.	$x_{a-}$ , Mole Fract. a-pinene in liquid calcd.	$y_{a-}$ , Mole Fract. a-pinene in vapor calcd.	$y_{a-}$ , Mole Fract. a-pinene in vapor obs.	Vapor Dev.
52.6	20.39	14.20	0.937	0.955	0.950	0.005
53.0	20.79	14.48	0.875	0.909	0.900	0.009
54.0	21.80	15.21	0.727	0.792	0.780	0.012
55.0	22.87	15.98	0.583	0.667	0.662	0.005
55.5	23.41	16.37	0.516	0.603	0.601	0.002
56.0	23.97	16.77	0.449	0.538	0.533	0.005
57.0	25.12	17.60	0.319	0.401	0.388	0.013
58.0	26.32	18.47	0.195	0.256	0.238	0.018
59.0	27.56	19.37	0.077	0.106	0.095	0.011
59.4	28.14	19.74	0.031	0.044	0.039	0.005

## Summary

The densities, refractive indices and optical rotations for a- and B-pinene and their mixtures have been determined.

The vapor pressure-temperature relations of a- and B-pinene were measured in the range of 15 to 80 mm.

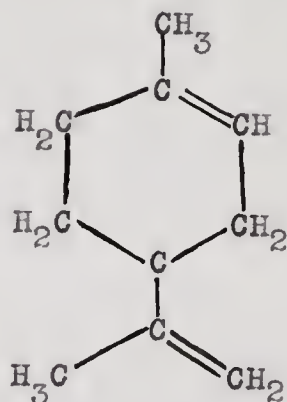
The vapor-liquid equilibrium composition data for mixtures of a- and B-pinene at 20 mm. pressure have been determined.

### CHAPTER III. THE THERMAL ISOMERIZATION OF $\alpha$ -PINENE

In 1853 Berthelot(24) heated French turpentine in sealed tubes at  $250^{\circ}$  for 10 hours. Polymerization occurred, accompanied by a change in rotation, and he noted that there was no gas formation. Wallach(25) found that  $\alpha$ -pinene formed dipentene(III) and some polymerized material when heated at  $250$ - $270^{\circ}$ .

The first rate determinations of this reaction were made by D. F. Smith(26). He determined the rate by heating sealed tubes of  $\alpha$ -pinene in a temperature controlled oil bath and measuring the rate of

decrease of the optical rotation of the reacting mixture. The temperature range was  $184$ - $237^{\circ}$ . Smith made most of his determinations by putting just enough  $\alpha$ -pinene in the tubes so that it was present in the gas phase only, at the temperatures of the experiment. Some determinations were made with  $\alpha$ -pinene in various solvents. In only one tube did  $\alpha$ -pinene remain in the liquid phase. This rate was determined at



Dipentene  
(III)

184.6° and was found to be of the same order of magnitude as the rate in the gas phase. He found the reaction to be of first order and assumed it to be a racemization of the  $\alpha$ -pinene. Smith distilled the partially reacted mixture from the tube in which the  $\alpha$ -pinene remained in the liquid phase and found its boiling point to be about 4° higher than that of the original mixture. The first part of the distillate had an optical activity 20% higher than that of the mixture but lower than that of the original  $\alpha$ -pinene. To account for this he explained that in all probability "a small fraction of the changes of one active variety of pinene to the opposite variety is accompanied by rearrangement of the molecule to form a high-boiling substance, which judging from the literature, should be limonene."

Conant and Carlson(27) proved that dipentene was formed in this reaction both in the liquid and the vapor phase at about 200°. They were unable to fractionate known mixtures of  $\alpha$ -pinene and dipentene with any efficiency through the columns at their disposal and resorted to measuring the amount of hydrogen absorbed by the reaction mixtures in order to determine the amount of dipentene formed. The increase in the amount of hydrogen absorbed was found to vary linearly with the decrease in optical rotation of the reaction mixture although the percentage error of a single determination was rather high. The lighter boiling fractions

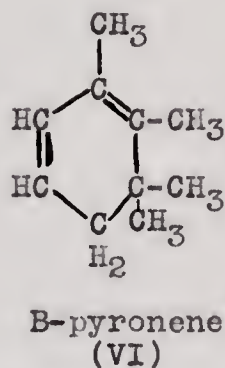
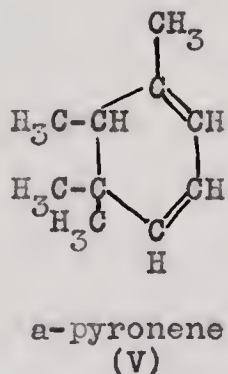
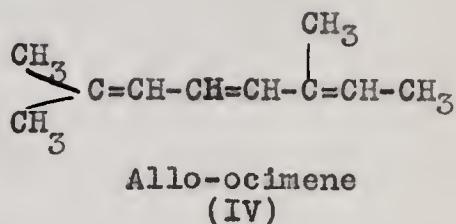


of the pyrolysate yielded a crystalline tetrabromide corresponding to that of dipentene. In addition they noted that an appreciable amount of polymerized material was obtained in the tubes in which the reaction went nearly to completion. Kassel(28) pointed out that on the basis of the results of Conant and Carlson the rate constants for the isomerization of  $\alpha$ -pinene to dipentene would be twice those calculated by Smith for the racemization of  $\alpha$ -pinene.

Thurber and Johnson(29), in an attempt to show that different isomers of  $\alpha$ -pinene exist, determined the energies of  $\alpha$ -pinene from two different sources. They followed the procedure of Smith. An appreciable difference in the energies of activation was found. However, this could have been due to impurities present in the samples of  $\alpha$ -pinene used. Upon fractionating approximately 20 cc. samples of reaction mixture they found that most of each sample distilled above  $159^{\circ}$  at atmospheric pressure, which was higher than the boiling point of the substrate, and hence concluded that the reaction was not a simple racemization.

In reviewing the results of the studies of this reaction prior to 1931 it should be noted that efficient fractionating columns were unavailable both for the purification of the substrate,  $\alpha$ -pinene, and for the analysis of the products.

Since that time some interesting results have been obtained on passing  $\alpha$ -pinene vapors through hot tubes at various temperatures. At 240-250° Arbuzov(30) found that as much as 26% of allo-ocimene(IV) was formed. Dupont and Dulou(31) using a copper tube packed with copper gauze obtained at these temperatures not only allo-ocimene and dipentene but also  $\alpha$ -pyronene(V) and B-pyronene(VI), which they characterized. Goldblatt and Falkin(32) isomerized d- $\alpha$ -pinene in an all glass apparatus and at 375° obtained about 12%  $\alpha$ - and B-pyronene, 42% dipentene and 40% allo-ocimene.



In view of these facts and with the previously described spiral screen fractionating columns available it seemed advisable to re-investigate the kinetics of the

liquid phase thermal isomerization of  $\alpha$ -pinene within the temperature range used by Smith(26). As this investigation proceeded it became evident that a more complete study of the over-all reaction should include a study of the polymerization of allo-ocimene.

### Experimental

Purification of reactants. A commercial grade of d- $\alpha$ -pinene from wood turpentine was carefully fractionated through a five foot length of spiral screen column of 37 mm. (1.45 inch) inside diameter. This necessitated the separation of  $\alpha$ -pinene from a slightly lower boiling fraction and from camphene which boils about 3° higher than  $\alpha$ -pinene. The fact that the rotation and the refractive index of the  $\alpha$ -pinene obtained varied slightly indicates that traces of impurities were not removed. However, the amounts of these impurities was insufficient to appreciably affect the results.

The allo-ocimene<sup>1</sup> was fractionated in 200 cc. batches through a four foot spiral screen column (inside diameter 10 mm. (0.40 inch)). The small amount of dipentene initially present in the samples and an intermediate fraction boiling at 75-77° at 10 mm., were discarded.

These compounds had the following range of physical

<sup>1</sup>Samples furnished through the courtesy of Naval Stores Research Laboratory, U.S.D.A. and of Southern Pine and Chemical Company.



constants:

$\alpha$ -pinene: b.p.<sup>20.0 mm</sup> 52.3°;  $a_D^{25}(2 \text{ dm.})$  +57.52°- +58.26°;

$n_D^{25.0}$  1.4631-1.4632.

allo-ocimene: b.p.<sup>10 mm</sup> 77-78°;  $d_4^{25.0}$  0.8050-0.8056;

$n_D^{25.0}$  1.5418-1.5424.

Apparatus. The sealed tubes of liquid were heated in a well insulated bath containing 5 gallons of oil agitated by two motor stirrers. Hydrogenated cottonseed oil, which was used at first, gradually polymerized and was replaced by white paraffin oil. The temperature of the bath was maintained constant by means of an Aminco Metastatic Thermoregulator connected to a vacuum tube-relay circuit developed by Huntress and Hershberg(33). Heat was supplied by two 250 watt blade heaters, one connected to the temperature control circuit and the other directly to the current source. A Beckmann thermometer placed in the bath showed an average variation of  $\pm 0.03^\circ$  and a maximum variation of  $\pm 0.04^\circ$ . The Beckmann thermometer showed that the average temperature of the bath did not change during the course of the heating. The bath temperature measurements were based on a thermometer calibrated by the U.S. Bureau of Standards (reading directly to  $0.1^\circ$ ). The temperatures used in the experiments were 189.5° and 204.5°.

Two spiral screen columns of 10 mm. (0.40 inch) inside diameter, four feet in length, were used to analyze the reaction mixtures. Ice water at 4-12°C. was circulated through the column head condensers. In addition, ice-HCl traps were placed in the system between each column and the manostat. Very little condensate was collected in the traps (usually less than 0.1 gm.). All fractionations were made at pressures between 10 and 20 mm.

Preliminary Procedure. In determining the amount of  $\alpha$ -pinene to be used for each reaction two factors were considered. The volume should be small enough that the liquid could be contained in a sealed glass tube capable of withstanding the pressures developed at the temperatures used but large enough that the amounts of material obtained between the pure fractions during the fractional distillations would have a small effect on the quantitative estimation of the components. It was found that lengths of heavy-walled Corning G-1 glass tubing of 27 mm. (1.08 inches) inside diameter could be purchased for constructing the tubes. To attain complete immersion in the oil bath these tubes could be only 10-11 inches long. Since 2-3 inches of free space should be left above the liquid in the tube, the volume to be filled with liquid would be 90-100 cc. In every case 94 cc. (80 gm.) of  $\alpha$ -pinene was placed in a tube.

The amount of allo-ocimene in each sealed tube for the separate polymerization study was limited by the small amount of allo-ocimene available. Samples of 17.5-20 cc. (14-16 gm.) of allo-ocimene were placed in 35 cc. tubes made from 20 mm. (0.8 inch) inside diameter glass tubing.

A sealed tube containing 94 cc. (80 gm.) of  $\alpha$ -pinene and an enclosed thermometer (which read about 0.6° low) was used to measure the rate of heating and of cooling of the  $\alpha$ -pinene under the conditions used. The data are given in Table 10, page 42. To measure the rate of heating the tube was placed in the oil bath for varying lengths of time and then withdrawn and the temperature of the liquid observed. The tube was allowed to cool to room temperature between each determination and the time recorded is the total time taken for the tube to attain the temperature indicated in the table. An additional 250 watt heater was turned on during the interval that the tube was being heated to temperature in order to counteract the cooling of the oil by the tube.

The rate of cooling was determined by removing the tube from the bath after it had reached constant temperature and observing the temperature of the liquid in the tube at various time intervals. The times recorded are the total time taken for the tube to cool from the bath temperature to the observed temperature.



Table 10

Rates of Heating and cooling of  $\alpha$ -PineneA. Temperature =  $189.5^{\circ}\text{C}$ .

<u>Heating</u>		<u>Cooling</u>	
Time min.	Temperature $^{\circ}\text{C}$ .	Time min.	Temperature $^{\circ}\text{C}$ .
0	26	0	188.8
4	169	1	178
6	180	2	168
8	186.5	3.5	151
11	188.8	4.5	142

B. Temperature =  $204.5^{\circ}\text{C}$ .

<u>Heating</u>		<u>Cooling</u>	
Time min.	Temperature $^{\circ}\text{C}$ .	Time min.	Temperature $^{\circ}\text{C}$ .
0	25	0	204
5	186	1	195
7	196	2	183
9	202	3	175
12	204	4	165
		5	156
		6	147

Table 11

## Rates of Heating and Cooling of Allo-ocimene

A. Temperature =  $189.5^{\circ}\text{C}$ .

<u>Heating</u>		<u>Cooling</u>	
Time min.	Temperature $^{\circ}\text{C}$ .	Time min.	Temperature $^{\circ}\text{C}$ .
0	25	0	188.8
2	170	1	175
4	186	2	160
5	188	3	146
6	188.8		

B. Temperature =  $204.5^{\circ}\text{C}$ .

<u>Heating</u>		<u>Cooling</u>	
Time min.	Temperature $^{\circ}\text{C}$ .	Time min.	Temperature $^{\circ}\text{C}$ .
0	25	0	204
3	195	1	187
4	201	2	171
5	203	3	155
6	204	4	141
8	204		

The rate of cooling is so rapid that no appreciable reaction will occur after the tube is removed from the bath. At each temperature, an appreciable amount of reaction should occur about five minutes after the tube is immersed in the bath. However the final temperature is not reached for another six or seven minutes. In each case a correction of about eight minutes should be allowed and so the time of heating of the  $\alpha$ -pinene tubes was recorded as starting eight minutes after the tubes were immersed in the oil bath. This correction is of no significance for tubes heated more than 25 hours.

Similar experiments with 20 cc. (16 gm.) of allo-ocimene in a sealed tube with an enclosed thermometer showed that at each temperature six minutes were required to raise the temperature of the liquid to that of the bath. Based on the heating data in Table 11, page 43, the time of heating of the tubes of allo-ocimene was recorded as starting 4 minutes after the tubes were inserted in the bath.

Procedure. The 94 cc. portions of freshly distilled  $\alpha$ -pinene were placed in 130 cc. tubes made from the Corning G-1 glass tubing. These tubes had been sealed at one end and had a tubular opening of 5 mm. (0.2 inch) inside diameter at the other. Each filled tube was connected to a vacuum line at 3-4 mm. and evacuated for five minutes.



The tubes were then sealed under vacuum.

The 17.5-20 cc. portions of freshly distilled allo-ocimene were placed in the 35 cc. tubes which were evacuated and sealed in the same manner as described for the tubes of  $\alpha$ -pinene.

After these sealed tubes had been placed in the oil bath and heated for the desired length of time, they were opened and analyzed. The amount to be fractionated was weighted. During the distillation all fractions were collected in 15-20 cc. receivers which had been weighed previously. When a fraction was cut by removing the receiver from the head it was weighed and the weight of the fraction determined by difference.

Identification of Products. Four major components were found in the mixtures: unreacted  $\alpha$ -pinene, dipentene, allo-ocimene, and a polymer. Upon the fractionation of the mixture the polymer was left in the kettle and was weighed.

$\alpha$ -Pinene Fraction: The recovered  $\alpha$ -pinene had virtually the same physical properties as the original with the exception of optical rotation. In the tubes which had little  $\alpha$ -pinene left it was sometimes difficult to recover pure fractions of  $\alpha$ -pinene but in most cases this was done. There can be little doubt that the recovered material was mainly  $\alpha$ -pinene. For example, the first fraction of Tube No. 14, in which at least 95% isomerization had occurred,

was a 2 cc. portion, b.p. (21 mm.) 52.8-53.2,  $n^{25}_D$  1.4630,  $d^{25}_4$  0.8525,  $a^{25}_D$  (2 dm.) +20.46°. A nitrosyl chloride was made by the method of Thurber and Thielke(33) by adding 3 cc. of 90% methyl alcohol and 2.5 cc. of isoamyl nitrite to it. This mixture was placed in a flask equipped with a mechanical stirrer and maintained at -10° to -20° while 5 cc. of 4.7 N HCl in 90% methyl alcohol were slowly added over a period of 40 minutes. The solution had a blue-green color and a small amount of the derivative was suspended in it. This was filtered in a funnel which had been cooled in the ice-box, and dried between clay plates. It melted 101-103°. Crystallization from benzene yielded a small amount melting with decomposition at 104-105° C. The nitrosochloride of  $\alpha$ -pinene was reported originally by Tilden and Shenstone(34) as melting at 103°. However it was noted by Tilden(35) at a later date that recrystallization of this compound raises the melting point from 2° to 12° depending on the solvent. Simonsen(36) states that since the melting is accompanied by decomposition, the melting point varies with the rate of heating and is usually found to be about 105-108°.

Dipentene Fraction: All of the dipentene from the tubes heated at 189.5° was combined and fractionated. It contained little impurity. The main portions had the physical properties:

b.p.(10 mm.) 59°;  $d^{25}_4$  0.8387;  $n^{25}_D$  1.4702;  $a^{25}_D$ (2 dm.) -4.60°.

The dipentene was identified by its tetrabromide. 7.5 gm. were dissolved in 60 cc. glacial acetic acid and 6 cc. (17.6 gm.) of bromine were added slowly with constant shaking. When all but 0.3 cc. had been added the color of the solution began to redden but the remainder of the bromine was added. The solution was allowed to stand for two days during which the precipitate formed. It was filtered from the solution, washed with acetic acid and dried. After recrystallization from methyl alcohol the crystals were dried between clay plates. They melted 124-125°. Wallach(37) first prepared this compound and reported a melting point of 125°. Goldblatt and Palkin(32) reported a melting point of 124.5-125.5°.

Fraction Intermediate between a-Pinene and Dipentene. 2-7% (1.5-5 gm.) of each reaction mixture boiled between a-pinene and dipentene. This portion no doubt contained mainly a-pinene and dipentene. There was some evidence of the presence of other compounds, particularly in those tubes which had reacted for the longer times. In these tubes an appreciable fraction of b.p. 53-60° (20 mm.) was sometimes obtained. This fraction could contain a small amount of camphene which might have been present in the original a-pinene and also a small amount of a-pyronene. Dupont and Dulou(38) give for a-pyronene a boiling point of 43°(11 mm.) and a refractive index (25°) of 1.4665. However, three attempts to make the maleic anhydride addition product of a-pyronene from some of these fractions were unsuccessful.



For the fraction of b.p. 60-72° (20 mm.) the refractive index was sometimes too high for that of dipentene; in the case of Tube No. 14, 1.0 gm. was obtained with an index of 1.4727. Dupont and Dulou(38) list the refractive index of B-pyronene which boils in this range as 1.4747. However an attempt to obtain a maleic anhydride addition product from this fraction was unsuccessful. The second fractions of Tubes No. 29 and 30 were combined (3 gm.;  $n_D^{25}$  1.4710; b.p. (20 mm.) 57-72°). From this a maleic anhydride addition product was made by adding 2 gm. of maleic anhydride and heating the mixture on the water bath for one hour. Upon cooling a gum separated from the liquid phase. The gum was washed with water and crystallized from methanol. It melted at 157-158°. Dupont and Dulou(38) found for the maleic anhydride addition product of B-pyronene a melting point of 154°. Goldblatt and Palkin(32) list it as 163-164°.

Allo-ocimene Fraction: The allo-ocimene was seldom obtained pure in these fractionations. The refractive indices (25°) were in the range 1.5330-1.5410. Only 1-3% of each mixture was found to boil between pure dipentene and the allo-ocimene obtained. This intermediate portion was combined with the allo-ocimene portion for all the tubes heated at 189.5° and the mixture fractionated. There were obtained 15 gm. of dipentene, 3.2 gm. of intermediate fraction and 29 gm. of allo-ocimene, b.p. (11 mm.) 76-79°;  $n_D^{25}$  1.5408-1.5424;  $d_4^{25}$  0.8068-0.8083. From this distillation it is obvious that no appre-

ciable amount of compound is formed boiling between dipentene and the allo-ocimene. The allo-ocimene portion had a boiling range which could not be attributed to the presence of dipentene as may be seen from the refractive index and density ranges. Similar behavior was noticed during the fractionation of the commercial samples of allo-ocimene. However in these latter cases a much higher percentage of high boil-component was obtained.

The allo-ocimene was identified by its maleic anhydride addition product which was prepared by the method of Goldblatt and Palkin(32). 7.3 gm. of allo-ocimene ( $n_D^{25}$  1.5415) was added to 5.5 gm. of maleic anhydride in a test tube which was then suspended in a beaker of boiling water for 1.5 hours. The product was distilled at 190-192° at 9 mm. The yield (10 gm.) was washed with heptane and recrystallized from hexane. Large white crystals, m.p. 81.0-81.5°, were obtained. Arbuzov(30) reported a melting point of 81-82°, and Goldblatt and Palkin, after two recrystallizations from hexane, obtained crystals melting 83-84°.

Polymer: The polymer obtained had refractive indices (25°) varying from 1.5130 to 1.5230. In the tubes heated for the longer times this value was always close to 1.5190. A portion of the polymer ( $n_D^{25}$  1.5180,  $d_4^{25}$  0.8857) was distilled with the results given in Table 12, page 50.

Molecular weight determinations by the freezing point

depression method were made of fractions 2 and 3, using cyclohexane ( $n_D^{25}$  1.4233; f.p.  $5.90^\circ\text{C}$ .; molal f.p. depression  $20.0^\circ$ ) as the solvent. If the polymer were a dimer ( $\text{C}_{20}\text{H}_{32}$ ) the molecular weight would be 272. Four determinations on fraction 2 gave an average molecular weight of 262 with an average deviation of 0.75% and a maximum deviation of 1.90%. Two determinations on fraction 3 gave values of 284 and 285, respectively. From these results the polymer appears to be a dimer.

Table 12  
Fractionation of the Polymer

Fraction No.	Weight gms.	B.p. (8mm.)	$n_D^{25}$
1	2.4	120-165	1.5194
2	30.0	165-175	1.5177
3	2.5	224-226	1.5189
		(3-4 mm.)	
4	0.4	Residue	

Quantitative estimation of components.— The use of refractive index data to analyze the composition of each fraction collected seemed practicable. By careful fractionation not more than two of the major components should be present in each fraction. Refractive index-composition data for known mixtures of  $\alpha$ -pinene and dipentene were measured. The data are recorded in Table 13. Column 3 gives the correction to be added to the weight % in column 1 to obtain a straight line relation between  $n_D^{25}$  and the weight %. In view of the fact that a variation of 1.3% in



the concentration of dipentene is represented by a change of one part in the fourth decimal place of the refractive index and since the maximum deviation from a straight line in the observed data is 1.1% all analyses were based on a straight line relation.

Since a small percentage of other components (probably camphene,  $\alpha$ - and B-pyronene) is present in the range boiling between  $\alpha$ -pinene and dipentene an error exists in calculating the percentage of these latter components on the basis of refractive index. The refractive indices of camphene,  $\alpha$ - and B-pyronene are higher than that of  $\alpha$ -pinene and would tend to increase the calculated percentage of dipentene.

This is illustrated in the case of Tubes No. 29 and 30. These were heated at  $204.5^{\circ}$  for a length of time such that less than 0.5%  $\alpha$ -pinene should have remained. About 4% of each reaction mixture distilled at 20 mm. between  $53^{\circ}$  and the boiling point of dipentene ( $72^{\circ}$  at 20 mm.) and the refractive indices ( $25^{\circ}$ ) of these fractions were in the range 1.4680-1.4720. This should represent the maximum amount of impurity which has been calculated as dipentene. These lower boiling fractions no doubt contained some dipentene. Thus it is probably that the error in the determination of the dipentene for these tubes does not exceed 3%.

A small amount of camphene (about 0.5%) may be initially

present in the substrate. The pyronenes increase in amount with the time of heating until, at the virtual completion of the isomerization of  $\alpha$ -pinene, the pyronenes plus the camphene constitute about 3% of the reaction mixture. The total correction for the percentage of camphene and the pyronenes was obtained by assuming 0.5% of camphene and a linear increase in the pyronenes with respect to the amount of  $\alpha$ -pinene reacted, until at completion of the reaction 2.5% of the pyronenes are present. By subtracting this correction from the percentage of dipentene determined on the basis of refractive index a more accurate value of the dipentene concentration is obtained.

The percentage of  $\alpha$ -pinene should be little affected. It is believed that the  $\alpha$ -pinene can be estimated to  $\pm 1\%$  from refractive index measurements.

Similar data were obtained for mixtures of dipentene and allo-ocimene and are recorded in Table 14, page 53. The maximum deviation from a linear relation is about 1.3% dipentene at 40% dipentene. Such a small deviation when applied to mixtures of not over 10 grams would have no significant effect in the determination of the quantity of dipentene. Actually the weight of any fraction containing this mixture never exceeded 6 grams. Therefore all calculations of composition for mixtures of allo-ocimene and dipentene were made assuming a linear relation between refractive index and composition.

Table 13

Refractive Indices of Mixtures of  
 $\alpha$ -Pinene and Dipentene

Weight % Dipentene	$n^{25}_D$	Correction
00.0	1.4631	----
19.4	1.4644	-1.1
29.2	1.4651	-1.0
53.6	1.4669	0.0
81.8	1.4689	-0.1
100.0	1.4702	----

Table 14

Refractive Indices of Mixtures of  
 Allo-ocimene and Dipentene

Weight % Allo-ocimene ( $n^{25}_D$ 1.5415)	$n^{25}_D$	Correction
00.0	1.4702	----
14.3	1.4808	+0.6
24.9	1.4885	+0.8
40.7	1.4999	+1.3
56.7	1.5112	+0.5
71.1	1.5212	+0.5
83.2	1.5299	+0.6



In the fractionations of the reaction mixtures one to one and a half grams of material usually were unaccounted for. When the column and head were not immediately rinsed out following a distillation a white gummy solid formed in small amounts in the column head and sidearm. Allo-ocimene forms such a compound when exposed to the air and it is believed that most of the material unrecovered was allo-ocimene. To trace this loss of material and to check the applicability of the refractive index data to the analysis of the components, test mixtures of known composition were fractionated in the analytical columns. The analyses were made on the basis of refractive index as discussed above.

Table 15

Fractionation of Test Mixtures

	Wt. a-pinene			Wt. dipentene			Wt. allo-ocimene			Wt. polymer		
	act.	obs.	dev.	act.	obs.	dev.	act.	obs.	dev.	act.	obs.	dev.
1.	42.3	42.1	-0.2	14.5	14.6	+0.1	4.3	3.7	-0.6	4.4	4.2	-0.2
2.	9.8	9.6	-0.2	49.8	49.7	-0.1	5.5	3.2	-0.4	12.6	12.5	-0.1
3.	---	---		6.6	6.3	-0.3	3.1	2.2	-0.9	4.7	4.9	+0.2
4.	---	---		5.3	4.8	-0.5	2.1	1.4	-0.7	10.2	10.1	-0.1
	av. loss = 0.2			av. loss = 0.2			av. loss = 0.65			av. loss = 0.05		

The average losses are 0.05 gm. of polymer, 0.2 gm. of a-pinene, 0.2 gm. of dipentene and 0.65 gm. of allo-ocimene. To reduce the effect of the appreciable loss of allo-ocimene on the calculations a correction of 0.5 gm. was added to the observed weight of allo-ocimene in each analysis.

Isomerization of  $\alpha$ -Pinene. Duplicate tubes of  $\alpha$ -pinene were heated at  $189.5^{\circ}$  for periods of from 20.5 to 607 hours and at  $204.5^{\circ}$  for periods of from 7.33 to 267 hours. Tables 16 and 17, pages 56 and 57, give the physical properties of the reaction mixtures immediately after the tubes were opened.

The refractive indices and boiling points of the fractions obtained by distillation of these reaction mixtures are given in Tables 35-66 (appendix).

Effect of Heat on Allo-ocimene and Dipentene. Harries(39) reported that dipentene is unreactive when heated in sealed tubes at temperatures up to  $300^{\circ}$ . To verify this, two sealed tubes, each containing 14 gm. of the purified dipentene, were heated for four hours in an oil bath at  $245-255^{\circ}$ . Fractionation of the combined product yielded 26.6 gm. of unchanged dipentene and 0.3 gm. of a high-boiling residue ( $n_D^{25} 1.5007$ ).

A sealed tube containing 17 gm. of a mixture of 46% allo-ocimene and 54% dipentene was heated for four hours under the same condition. By fractionation of the products the dipentene was recovered unchanged. In addition, the products contained about 2% of a lower boiling fraction, 31% of polymer and 13% of unreacted allo-ocimene. From this it is apparent that the dipentene yields no products, that it is not appreciably involved in the formation of the polymer and that the allo-ocimene alone forms the polymer.

Table 16

## Physical Properties of Reaction Mixtures

Temperature = 189.5°

Tube No.	Time Heated Hours	% $\alpha$ -pinene unreacted	$n_D^{25}$	$a_D^{25}$ (2 dm.)	$d_4^{25}$
1	20.5	88.3	1.4658	+50.66	0.8506
2	20.5	88.3	1.4656	+50.80	0.8506
3	51.0	76.5	1.4692	+41.60	0.8488
4	51.0	76.3	1.4692	+41.50	0.8491
5	82.0	65.7	1.4722	+33.80	0.8481
6	82.0	64.2	1.4721	+33.80	0.8483
*40	130.0	50.5	1.4754	(-2.80)	0.8476
*41	130.0	50.2	1.4754	(-2.82)	0.8477
7	178.0	37.7	1.4780	+18.85	0.8476
8	178.0	37.2	1.4780	+18.90	0.8477
9	250.5	25.9	1.4805	+ 9.70	0.8479
10	250.5	25.8	1.4804	+10.00	0.8481
11	377.0	13.9	1.4828	+ 3.10	0.8490
12	377.0	14.0	1.4828	+ 3.05	0.8494
13	607.0	3.9	1.4852	- 1.43	0.8510
14	607.0	5.0	1.4849	- 1.52	0.8508

\*These tubes contained  $\alpha$ -pinene from gum turpentine,  
 b.p. 52.2° (20 mm.),  $n_D^{25}$  1.4631,  $d_4^{25}$  0.8542,  $a_D^{25}$  (2 dm.)  
 -6.49°.



Table 17  
Physical Properties of Reaction Mixtures  
Temperature = 204.5°

Tube No.	Time Heated Hours	% a-pinene unreacted	$n_D^{25}$	$a_D^{25}$ (2 dm.)
15	7.33	85.5	1.4678	+47.28
16	7.33	86.2	1.4677	+47.46
17	13.75	74.1	1.4708	+39.62
18	13.75	74.1	1.4708	+39.74
19	20.0	64.8	1.4734	+32.50
20	20.0	65.3	1.4732	+32.64
21	25.0	58.7	1.4745	+28.45
22	25.0	58.4	1.4746	+28.29
23	34.0	48.1	1.4772	+22.40
24	34.0	48.1	1.4771	+22.43
25	51.0	32.1	1.4806	+13.48
26	51.0	32.1	1.4806	+13.61
27	101.0	11.1	1.4852	+ 1.33
28	101.0	11.2	1.4853	+ 1.38
29	267.0	----	1.4869	- 2.18
30	267.0	----	1.4867	- 2.15

Arbuzov(30) heated allo-ocimene in a sealed tube for one hour at 250-300° and one-half hour at 320°. Upon fractionation he obtained 7 gm. of material boiling from 55° (14 mm) to 135° (4 mm) and 8 gm. of a polymer. Arbuzov reported that refractionation of the lower boiling portion yielded 5 gm. of a terpene, b.p. 57-58.5° (14 mm.),  $n_{D}^{25}$  1.4785,  $d_{4}^{22}$  0.8422. This terpene gave no crystalline tetrabromide nor nitrosite. He did not attempt to prepare the maleic anhydride addition product. From the similarity of the physical properties of this terpene to those reported by Dupont and Dulou(38) for B-pyronene it was suspected that this might be B-pyronene formed by the cyclization of allo-ocimene. To check this point, 60 gm. of allo-ocimene were heated at 300-310° for two and a half hours in a sealed tube. The products obtained were divided into four main fractions:

Fraction 1.	9%	b.p. (20 mm.) 43-57°	$n_{D}^{25}$ 1.4663
Fraction 2.	15%	b.p. (20 mm.) 57-69°	$n_{D}^{25}$ 1.4791
Fraction 3.	12%	b.p. (20 mm.) 69-90°	$n_{D}^{25}$ 1.4848
Fraction 4.	64%	Polymer	$n_{D}^{25}$ 1.5166

Before the analyses of these fractions were started Goldblatt(40) stated that he had already completed experiments proving that a- and B-pyronene are formed by the cyclization of allo-ocimene. Since Fractions 1 and 2 have physical properties which correspond to those of a- and B-pyronene,

respectively, maleic anhydride addition products were made of these two fractions.

4.5 gm. of Fraction 1 were added to 4 gm. of maleic anhydride and heated on a water bath for three hours. The product was distilled yielding 0.8 g. of oil, b.p. (12 mm.) 48-54°,  $n_D^{25}$  1.4668 and 3 gm. of a viscous material, b.p. (12 mm.) 202-204°. This latter fraction was probably the addition product of maleic anhydride with  $\alpha$ -pyronene. However, repeated attempts to recrystallize it from methanol were unsuccessful.

7.5 g. of Fraction 2 were added to 6 gm. of maleic anhydride and heated for one hour. Distillation of the mixture gave 6 gm. of an addition product, b.p. (12 mm.) 195-198°. This was crystallized from aqueous methanol. The crystals melted at 161-162°. Goldblatt and Palkin(32) reported a melting point of 163-164° for this derivative of B-pyronene.

These findings confirm the report of Goldblatt that allo-ocimene cyclizes to form the pyronenes.

Kinetics of the Isomerization. The quantitative analyses of the isomerization products of  $\alpha$ -pinene indicated that the amount of dipentene increased continuously. The monomeric allo-ocimene reached a maximum value when the  $\alpha$ -pinene was 40-75% isomerized and then slowly decreased, while the polymer continuously increased.



From these data it is probable that the dipentene and allo-ocimene are produced by simultaneous side reactions, and the polymer by a consecutive reaction from the allo-ocimene.

These two side reactions would each be expected to be first order. In a reaction of this order the rate is directly proportional to the concentration of the substrate, or, mathematically,

$$-dc/dt = kc \quad (11)$$

where  $c$  is the concentration of the substrate. If  $a$  is the initial concentration of the substrate, and  $x$  is the decrease in its concentration after time  $t$ , the amount of substrate remaining will be  $a-x$ . Then

$$-d(a - x)/dt = k(a - x) \quad (12)$$

$$-da/dt + dx/dt = k(a - x)$$

Since  $a$  is constant,

$$dx/dt = k(a - x)$$

$$\text{or, } dx/(a - x) = k(dt)$$

Integrating this:

$$-\ln(a - x) = kt + C \quad (13)$$

$$\text{At } t = 0, x = 0; \quad -\ln(a) = C$$

$$\text{Then: } \ln(a) - \ln(a - x) = kt$$

$$k = (1/t) \ln \frac{a}{a - x} = \frac{2.303}{t} \log \frac{a}{a - x} \quad (14)$$

Since the reaction tubes contained practically 100%  $\alpha$ -pinene, the rate of disappearance of  $\alpha$ -pinene may be

calculated at any given time,  $t$ , by letting  $a = 100.0$  and  $(a - x) =$  the percentage of  $\alpha$ -pinene unreacted at time  $t$ . For example, 64.1%  $\alpha$ -pinene was recovered from the reaction mixture of Tube No. 6, which had been heated 4920 minutes at  $189.5^\circ$ . Then

$$k' = \frac{2.303}{4920} \log \frac{100.0}{64.2} = 9.01 \times 10^{-5} \text{ min.}^{-1} \quad (15)$$

If  $k_1$  equals the rate of formation of dipentene, and  $k_2$  the rate of formation of allo-ocimene,  $k'$  above, the rate of disappearance of  $\alpha$ -pinene, is equivalent to  $k_1 + k_2$ :

$$dx/dt = k_1(a - x) + k_2(a - x) = (k_1 + k_2)(a - x) \quad (16)$$

By the above steps it may be derived that

$$k_1 + k_2 = \frac{2.303}{t} \log \frac{a}{a - x} \quad (17)$$

In order to evaluate  $k_1$  and  $k_2$  separately, consider the following:

$$\begin{array}{ll} \text{Rate of formation of dipentene} & = k_1(a - x) \\ \text{Rate of formation of allo-ocimene} & = k_2(a - x) \end{array}$$

Then, at any time, the ratio of the concentrations of dipentene to allo-ocimene would be equal to  $k_1/k_2$  provided no other complications were involved. In this particular reaction the allo-ocimene polymerizes rather rapidly, and the total amount of allo-ocimene that has been formed in the reaction at any time is equal to the sum of the allo-

ocimene and the polymer present in the reaction mixture.  
so, at any given time,

$$\frac{k_1}{k_2} = \frac{\text{Dipentene}}{\text{Allo-ocimene} + \text{Polymer}} \quad (18)$$

Tables 18 and 19, pages 63 and 64, summarize the data for the tubes which were heated at 189.5° and 204.5°, respectively. Column 4 lists the values of  $k'$  ( $= k_1 + k_2$ ) calculated from the % of  $\alpha$ -pinene unreacted. Column 5 lists the calculated total percentage of the compounds boiling between  $\alpha$ -pinene and dipentene. In column 9 are the values of  $k_1/k_2$  calculated from the ratios of dipentene to allo-ocimene plus polymer found in each analysis.

$$\text{Now } \frac{k_1 + k_2}{k_2} = \frac{k_1}{k_2} + 1 \quad (19)$$

$$\text{and } k_1 + k_2 = k' = k_2 \left( \frac{k_1}{k_2} + 1 \right)$$

$$\text{Hence } k_2 = \frac{k'}{\left( \frac{k_1}{k_2} + 1 \right)} \quad (20)$$

Since  $k'$  and  $k_1/k_2$  are both calculated from the experimental data, the individual values of  $k_1$  and  $k_2$  can be determined. The following calculations are made using the average value of  $k'$  and  $k_1/k_2$ :

$$\text{At } 189.5^\circ - \quad k_2 = \frac{8.99 \times 10^{-5}}{2.14 + 1.00} = \frac{8.99}{3.14} \times 10^{-5}$$

$$k_2 = 2.86 \times 10^{-5} \text{ min.}^{-1}$$



Table 18

Summary of Results and Calculations  
Temperature = 189.5°

Tube No.	Time min.	% a-pinene unreacted	$k' \times 10^5$ min. <sup>-1</sup>	% other compds.	% di-pentene	% allo-ocimene	% polymer	$k_1/k_2$
1	1230	88.4	10.03	0.8	7.1	1.6	2.3	1.87
2	1230	88.3	10.12	0.8	6.7	3.0	1.3	(1.56)
3	3060	76.5	8.76	1.1	15.3	4.1	3.0	2.15
4	3060	76.3	8.80	1.1	15.1	4.9	2.6	2.01
5	4920	65.7	8.54	1.4	22.2	5.0	5.7	2.07
6	4920	64.2	9.01	1.4	23.1	5.5	5.8	2.05
40	7800	50.5	8.75	1.7	32.5	5.8	9.4	2.14
41	7800	50.2	8.84	1.7	32.9	6.1	9.2	2.15
7	10680	37.7	9.14	2.1	42.4	5.6	12.2	2.38
8	10680	37.2	9.26	2.1	42.6	6.4	11.7	2.35
9	15030	25.9	9.01	2.4	48.8	6.0	16.9	2.13
10	15030	25.8	9.02	2.4	49.0	5.8	17.0	2.15
11	22620	13.9	8.73	2.6	57.3	5.2	21.0	2.18
12	22620	14.0	8.70	2.6	57.4	5.0	21.0	2.20
13	36420	3.9	8.91	2.9	63.4	3.9	25.8	2.13
14	36420	5.0	8.23	2.9	62.9	3.7	25.5	2.15
		Av. $k' = 8.99 \times 10^{-5}$				Av. $k_1/k_2 = 2.14$		
		Av. Dev. = $0.33 \times 10^{-5}$				Av. Dev. = 0.08		
		% Av. Dev. = 3.7%				% Av. Dev. = 3.7%		

Table 19

Summary of Results and Calculations  
Temperature = 204.5°

<u>Tube No.</u>	<u>Time min.</u>	<u>% a-pinene unreacted</u>	<u>k'x10<sup>5</sup> min.<sup>-1</sup></u>	<u>% other compds.</u>	<u>% di-pentene</u>	<u>% allo-ocimene</u>	<u>% polymer</u>	<u>k<sub>1</sub>/k<sub>2</sub></u>
15	440	85.5	35.6	0.8	9.1	4.0	0.6	1.97
16	440	86.2	33.8	0.8	8.1	4.1	0.8	(1.65)
17	825	74.1	36.3	1.1	16.6	6.6	1.6	2.02
18	825	74.4	35.9	1.1	16.1	6.9	1.5	1.92
19	1200	64.8	36.2	1.4	22.5	7.8	3.5	1.99
20	1200	65.3	35.5	1.4	22.4	7.6	3.3	2.05
21	1500	58.7	35.5	1.5	26.5	8.3	4.0	1.99
22	1500	58.4	35.9	1.5	26.8	8.4	4.9	2.02
23	2040	48.1	35.9	1.8	33.4	8.5	8.2	2.00
24	2040	48.1	35.9	1.8	33.5	8.5	8.1	2.02
25	3060	32.1	37.1	2.2	44.0	8.0	13.7	2.03
26	3060	32.1	37.1	2.2	44.0	8.4	13.3	2.03
27	6060	11.1	36.3	2.7	57.5	6.9	21.8	2.00
28	6060	11.2	36.1	2.7	57.3	6.8	22.0	1.99
29	16020	----		3.0	64.4	4.9	27.7	1.97
30	16020	----		3.0	64.2	5.0	27.8	1.96
		Av. k' = 35.9x10 <sup>-5</sup>				Av. k <sub>1</sub> /k <sub>2</sub> = 2.00		
		Av.Dev. = 0.5x10 <sup>-5</sup>				Av. Dev. = 0.025		
		% Av.Dev. = 1.4%				% Av. Dev. = 1.3%		

$$\text{and } k_1 = k' - k_2 = (8.99 - 2.86) \times 10^{-5}$$

$$k_1 = 6.13 \times 10^{-5} \text{ min.}^{-1}$$

$$\text{At } 204.5^\circ - \quad k_2 = \frac{3.59 \times 10^{-4}}{2.00 + 1.00} = \frac{3.59}{3.00} \times 10^{-4}$$

$$k_2 = 1.20 \times 10^{-4} \text{ min.}^{-1}$$

$$\text{and } k_1 = k' - k_2 = (3.59 - 1.20) \times 10^{-4}$$

$$k_1 = 2.39 \times 10^{-4} \text{ min.}^{-1}$$

#### Decrease in Optical Rotation of the Unreacted $\alpha$ -Pinene.-

A study of a model of the  $\alpha$ -pinene molecule shows that it is necessary to break at least two carbon to carbon valence bonds, shift two hydrogen atoms, and then join the bonds in a different position before it can be changed to the mirror image. Such a step would seem improbable as the molecule would be broken up completely during the transformation and apparently could form allo-ocimene more readily than it could re-form  $\alpha$ -pinene.

Attempts have been made unsuccessfully by various workers to prove or disprove the existence of four optical isomers of  $\alpha$ -pinene since it has two asymmetric carbon atoms. However the study of the model of the  $\alpha$ -pinene molecule indicates that these two carbon atoms, the carbon links between the six-membered ring and the cyclobutane ring, are so bound to the molecule that only two optical isomers seem possible.

Nevertheless, during the heating the optical activity of the unreacted  $\alpha$ -pinene slowly decreases at a rate which



fits a first order reaction equation with an average deviation of 9.7% at 189.5° and of 6.5% at 204.5°. The constants, measuring the rate of decrease to zero optical rotation of the  $\alpha$ -pinene at the two temperatures, are given in column 5, Tables 20 and 21, pages 67 and 68. They were calculated by the formula:

$$k_3' = \frac{2.303}{t} \log \frac{a_1}{a_t} \quad (21)$$

where  $a_1$  is the initial observed angle of rotation of the  $\alpha$ -pinene and  $a_t$  is its' observed angle of rotation at time  $t$ , using a 2 dm. tube.

The  $\alpha$ -pinene from gum turpentine, heated in Tubes No. 40 and 41, which has a negative rotation, also underwent a decrease in its optical activity. Its' rate of decrease of optical activity is of the same order of magnitude as that of the d- $\alpha$ -pinene but the determination of the exact value is subject to large error because of the small rotation of the sample.

If the recovered material with the lowered rotation is pure  $\alpha$ -pinene, and this seems to be the case, the  $\alpha$ -pinene probably does racemize. In breaking its bonds to form allo-ocimene the  $\alpha$ -pinene may form an intermediate which could produce allo-ocimene or recyclize to form  $\alpha$ -pinene. Upon recyclizing this intermediate could form either of the optical isomers with equal ease resulting in a racemic mixture. The rate constant for the racemization of  $\alpha$ -pinene would be one-half the value of  $k_3'$ , since, starting with the pure d- $\alpha$ -pinene,

Table 20

Decrease in Optical Rotation of  $\alpha$ -Pinene  
Temperature =  $189.5^{\circ}$

<u>Tube No.</u>	<u>Time min.</u>	<u><math>a_1</math> (2 dm.)</u>	<u><math>a_t</math> (2 dm.)</u>	<u><math>k_1 \times 10^5</math> min.<sup>-1</sup></u>	<u><math>k_2 \times 10^6</math> min.<sup>-1</sup></u>
1	1230	+58.02	+56.82	1.7	8.5
2	1230	+58.26	+57.00	1.8	8.9
3	3060	+58.00	+54.75	1.9	9.5
4	3060	+58.00	+54.79	1.9	9.3
5	4920	+58.02	+52.25	2.1	10.7
6	4920	+57.52	+53.00	1.7	8.3
7	10680	+57.94	+47.38	1.9	9.4
8	10680	+57.94	+47.39	1.9	9.4
9	15030	+58.12	+43.00	2.0	10.0
10	15030	+57.90	+42.66	2.0	10.2
11	22620	+57.75	+36.00	2.1	10.5
12	22620	+57.75	+35.87	2.1	10.6
13	36420	+58.28	+21.00	1.4	7.2
14	36420	+58.00	+20.46	1.4	7.0
40	7800	-6.49	-5.92	(1.2)	(6.0)
41	7800	-6.49	-5.90	(1.2)	(6.1)
				Average =	9.3
				Av. Dev. =	0.9
				% Av. Dev. =	9.7%

Table 21

Decrease in Optical Rotation of  $\alpha$ -Pinene  
Temperature =  $204.5^{\circ}$

<u>Tube No.</u>	<u>Time min.</u>	<u><math>a_1</math> (2 dm.)</u>	<u><math>a_t</math> (2 dm.)</u>	<u><math>k_1 \times 10^5</math> min.<sup>-1</sup></u>	<u><math>k_2 \times 10^6</math> min.<sup>-1</sup></u>
15	440	+58.00	+56.02	7.9	4.0
16	440	+58.00	+56.13	7.5	3.7
17	825	+58.00	+54.33	7.7	3.9
18	825	+58.00	+54.49	7.6	3.8
19	1200	+57.98	+52.60	8.1	4.1
20	1200	+57.98	+52.31	8.6	4.3
21	1500	+57.88	+50.57	9.0	4.5
22	1500	+57.95	+50.78	8.6	4.3
23	2040	+57.88	+48.50	8.7	4.4
24	2040	+57.88	+48.78	8.4	4.2
25	3060	+58.12	+45.75	7.8	3.9
26	3060	+58.12	+45.85	7.8	3.9
27	6060	+57.45	+32.05	9.6	4.8
28	6060	+57.76	+33.35	9.1	4.6
				Average = <u>4.2</u>	
				Av. Dev. = 0.27	
				% Av. Dev. = 6.4%	



only half of the  $\alpha$ -pinene molecules must change their rotation in order to form a racemic mixture(26,28). The racemization rate constants of  $\alpha$ -pinene,  $k_3$ , are given in column 6, Tables 20 and 21..

Polymerization of Allo-ocimene. From the data previously obtained, it would seem that allo-ocimene should form a dimer by a second order reaction. Preliminary experiments indicated that the polymer from pure allo-ocimene was more homogeneous than that formed from the products of the  $\alpha$ -pinene isomerizations. The former boiled at 173-176°C. (9 mm.) and had a refractive index range (25°) of 1.5208-1.5212. Three molecular weight determinations of this sample of polymer gave values of 260, 260 and 262.

In studying this reaction, the sealed tubes of allo-ocimene were heated for varying lengths of time and then were opened and the allo-ocimene was separated from its dimer in the spiral screen analytical columns previously described. A known weight of the mixture was taken for the separation of the components and the polymer remaining in the flask was weighed. The % polymer formed was calculated by dividing the weight of polymer by the total weight of mixture taken. The data are given in Tables 22 and 23, pages 74 and 75. The  $n^{25}_D$  for the allo-ocimene recovered from each tube is given in column 4 of these tables. In general this value tends to decrease for those tubes heated for the longer times. This decrease in refractive

index is probably due to the formation of small amounts of a- and B-pyronene from the allo-ocimene. However, a complete interpretation of these data must await further study.

Unexpectedly, it was found that the dimerization does not go to completion. This suggested either that the allo-ocimene contained a component that will not polymerize or that the dimer was in equilibrium with its monomer. The recovered allo-ocimene (2 gm.) from Tubes No. 66 and 67 was heated 24 hours at 189.5°. The product was almost completely polymer, b.p. (10 mm.) 170-178°,  $n_D^{25}$  1.5190. The allo-ocimene in Tube No. 68 was that recovered from tubes No. 58-59. Thus it is seen that the unreacted portion may be dimerized if separated from the dimer already formed.

Sealed tubes of the recovered polymer were heated to see if allo-ocimene could be obtained from it. These data are given in Table 24, page 76. The polymer recovered from Tube No. 90 was sealed in Tube No. 91 and heated for the same length of time. The same amount of allo-ocimene was recovered in each case. There can be no doubt that this is an equilibrium reaction.

The rate constants for the formation of the dimer, calculated from formula (30), derived from the following considerations.

The reaction is of the type



If no B is initially present, then at any time,

$$dx/dt = k_4(a - x)^2 - k_5x \quad (22)$$

where a is the initial concentration of A in moles/liter and x

is the number of moles/liter reacted at time  $t$ .

At equilibrium,  $k_4(a - q)^2 = k_5q$  (23)

where  $q$  is the amount of A reacted when equilibrium is reached.

Then  $k_5 = k_4(a - q)^2/q$

and from (22)-

$$dx/dt = k_4(a - x)^2 - k_4(a - q)^2 x/q \quad (24)$$

$$dx/dt = k_4((a - x)^2 - (a - q)^2(x/q))$$

$$dx/dt = k_4(a^2 - 2ax + x^2 - (x/q)(a^2 - 2aq + q^2))$$

$$dx/dt = k_4(a^2 - 2ax + x^2 - a^2x/q + 2ax - xq)$$

$$dx/dt = k_4(a^2(1 - x/q) + x(x - q))$$

$$dx/dt = k_4((a^2/q)(q - x) - x(q - x))$$

$$dx/dt = (k_4/q)(q - x)(a^2 - xq) \quad (25)$$

Then-  $\frac{qdx}{(q - x)(a^2 - xq)} = k_4 dt$  (26)

Solving the left hand term of (26) by partial fractions,

Let  $\frac{q}{(q - x)(a^2 - xq)} = \frac{M}{(q - x)} + \frac{N}{(a^2 - xq)}$  (27)

where  $M$  and  $N$  are constants. Then

$$q = M(a^2 - xq) + N(q - x)$$

$$q = Ma^2 - Mxq + Nq - Nx$$

Equating coefficients of like powers of  $x$ ,

$$q = Ma^2 + Nq$$

$$0 = -Mq - N \quad \text{and} \quad N = -Mq$$

$$q = Ma^2 - Mq^2$$

$$M = q/(a^2 - q^2) \quad \text{and} \quad N = -q^2/(a^2 - q^2)$$

Therefore-  $\frac{q}{(q - x)(a^2 - xq)} = \frac{q}{(a^2 - q^2)(q - x)} - \frac{q^2}{(a^2 - q^2)(a^2 - xq)}$



$$\frac{q}{(a^2 - q^2)} \frac{dx}{(q - x)} - \frac{q^2}{(a^2 - q^2)} \frac{dx}{(a^2 - xq)} = k_4 \, dt$$

$$\frac{q}{(a^2 - q^2)} (-\ln(q-x)) - \frac{q^2}{(a^2 - q^2)} (-1/q) \ln(a^2 - xq) = k_4 t + C$$

Combining terms:

$$\frac{2.303q}{a^2 - q^2} \log \frac{(a^2 - xq)}{(q - x)} = k_4 t + C \quad (28)$$

$$\text{At } t = 0, x = 0 \text{ and } C = \frac{2.303q}{a^2 - q^2} \log \frac{a^2}{q} \quad (29)$$

So (28) becomes

$$k_4 = \frac{2.303}{t} \cdot \frac{q}{a^2 - q^2} \log \frac{q(a^2 - xq)}{a^2(q - x)} \quad (30)$$

Since second order reaction constants involve a concentration unit it is necessary to know the density of the allo-ocimene at the temperatures at which the reaction occurred. To determine this, 35 cc. of allo-ocimene were placed in a tube of 1 cm. inside diameter and sealed. The tube was placed in the oil bath at 204.5° for ten minutes and the level of the allo-ocimene in the tube marked. The liquid was then cooled to 25° and this level marked. After the tube was broken and the liquid removed, the increase in volume was found to be 19% by determining the weight of water in the tube when filled to each mark. Since the allo-ocimene has a  $d_4^{25}$  of 0.805 it follows that  $d_4^{204.5} = 0.805/1.19 = 0.68$ . By interpolation  $d_4^{189.5}$  is estimated to be 0.69.

The initial molar concentration,  $a$ , of allo-ocimene at 204.5° =  $dx1000/\text{m.w.} = 680/136 = 5.0$  moles/liter.

At 189.5° this value is  $690/136 = 5.1$  moles/liter.

The number of moles/liter of allo-ocimene reacted at equilibrium,  $q$ , equals (ax% allo-ocimene reacted at equilibrium). At 189.5° the average of Tubes No. 66, 67, 93 and 94 indicate that 89% allo-ocimene had reacted at equilibrium. Thus  $q = 5.0(0.89) = 4.5$  moles/liter.

At 204.5°, the average of Tubes No. 80, 81, 95, and 96 indicate that 88% allo-ocimene had reacted at equilibrium. Hence, at 204.5°,  $q = 0.88(5.1) = 4.5$  moles/liter.

The calculation of  $k_4$  by equation (30) may be illustrated with the data for Tube No. 54, which, when heated 408 minutes at 189.5° yielded 64% polymer. The units of concentration in the numerator and denominator cancel in the log term and fractions may be substituted directly in this part of the equation, where  $a = 1.00$ ,  $q = 0.89$ , and  $x = 0.64$ .

$$k_4 = \frac{2.303 \cdot 4.5}{408 (5.1)^2 - (4.5)^2} \log \frac{0.89(1 - 0.89(0.64))}{1.0(0.89 - 0.64)}$$

$$k_4 = 8.1 \times 10^{-4} \text{ liters/mole-min.}$$

The values of  $k_4$  are given in column 8, Tables 22 and 23, pages 74 and 75. From this it may be concluded that the data for the reaction has been correctly interpreted.

Several Diels-Alder reactions have been found to be reversible bimolecular associations of the same type as the dimerization of allo-ocimene. All of these Diels-Alder reactions involve "a 1:4 addition of an ethenoid to a butadienoid system" (41). The dimerization of allo-ocimene is quite probably the

Table 22

Reversible Polymerization of Allo-ocimene  
Temperature = 189.5°

a = 5.1 moles/liter

q = 4.5 moles/liter

Tube No.	Time Heated		Allo-ocimene Recovered	Wt. Mixture	Wt. Polymer	% Polymer	$k_4 \times 10^4$ liters/mole-min.
	min.	hr.	$n_D^{25}$	gm.	gm.		
50	108	1.80	1.5416	15.8	5.4	34	9.1
51	108	1.80	1.5417	16.6	5.3	32	7.9
52	254	4.23	1.5415	15.9	8.5	54	8.5
53	254	4.23	1.5419	15.9	8.4	53	8.3
54	408	6.80	1.5411	16.3	10.4	64	8.1
55	408	6.80	1.5415	16.1	10.4	65	8.5
56	720	12	1.5396	16.4	12.4	76	8.7
57	720	12	1.5410	16.3	12.3	76	8.7
58-59	1020	17	1.5412	32.0	25.6	80	7.8
68	1020	17	1.5392	5.5	4.2	76	
60	1440	24	1.5388	16.3	13.7	84	8.1
61	1440	24	1.5410	16.4	13.9	85	8.9
62	5990	66.5	1.5355	15.7	13.7	87	
63	5990	66.5	1.5377	15.7	13.7	88	
64	6780	113	1.5413	16.0	14.0	87.5	
65	8220	137	1.5381	15.5	13.4	86.5	
66	13260	221	1.5360	15.6	13.8	88.5	
67	14760	246	1.5340	15.7	14.1	90	
Average =							$8.4 \times 10^{-4}$
Av. Dev. =							0.35
% Av. Dev. =							4.2%



Table 23

Reversible Polymerization of Allo-ocimene  
Temperature = 204.5°

a = 5.0 moles/liter

q = 4.5 moles/liter

Tube No.	Time Heated		Allo-ocimene Recovered	Wt. Mixture	Wt. Polymer	% Polymer	$k_4 \times 10^4$ liters/mole-min.
	min.	hr.	$n_D^{25}$	gm.	gm.		
68	50	0.83	1.5419	13.7	4.4	32	23
69	50	0.83	1.5418	14.9	4.9	33	24
70	130	2.17	1.5415	12.9	7.0	54	22
71	130	2.17	1.5420	13.6	7.4	54	22
72	185	3.08	1.5413	15.4	10.0	65	26
73	185	3.08	1.5411	15.5	9.7	63	23
74	285	4.75	1.5389	14.4	10.2	71	22
75	285	4.75	1.5395	14.9	10.4	70	21
76	395	6.58	1.5393	15.3	11.5	75	20
77	395	6.58	1.5400	14.4	10.8	75	20
78	640	10.67	1.5360	14.9	12.0	81	19
79	640	10.67	1.5374	15.4	12.4	81	19
80	3480	58	1.5263	13.6	11.9	87.5	
81	5700	95	1.5260	14.4	12.5	87	

Average =  $\frac{22}{1}$   
 Av. Dev. = 1.5  
 % Av. Dev. = 6.8%

Table 24

## Decomposition of Polymer

<u>Tube No.</u>	<u>Time Heated hr.</u>	<u>Allo- ocimene Recovered n<sup>25</sup>D</u>	<u>Wt. Mixture gm.</u>	<u>Wt. Polymer gm.</u>	<u>% Polymer</u>
(Temperature = 189.5°)					
90	148	1.5396	17.3	15.9	92
91	148	1.5350	13.8	12.7	92
92	239	1.5423	16.6	14.9	90
93	390	1.5300	14.5	13.0	89.5
94	390	1.5415	14.8	13.1	88.5
(Temperature = 204.5°)					
95	95	1.5275	17.2	15.2	88.5
96	135	1.5267	18.2	16.0	88

same type of bimolecular association. It is believed that the allo-ocimene molecule furnishing a single double bond to the ring formation of the dimer reacts only at the middle double bond. If it should react at either of the end double bonds a conjugated system would be left free to react further and a chain polymerization would be expected to occur.

By determining the equilibrium constant of the reaction, the value of  $k_5$ , the rate of decomposition of the dimer to allo-ocimene may be calculated from the equation  $K_{eq.} = k_4/k_5$ . The density of the equilibrium mixtures at 25° in Tubes No. 66 and 80 was found to be about 0.875. To determine the density of the equilibrium mixture at 204.5° the method described for the determination of the density of allo-ocimene at this temperature was used. It was found to be 0.74. By interpolation, the density of the equilibrium mixture at 189.5° was calculated as 0.75.

$$K_{eq.} = \frac{(\text{polymer})}{(\text{allo-ocimene})^2}$$

At 189.5°,

$$K_{eq.} = \frac{\frac{0.89(0.75) \times 1000}{272}}{\left(\frac{0.11(0.75) \times 1000}{136}\right)^2} = 6.7 \text{ liters/mole}$$

$$k_5 = k_4/K_{eq.} = 8.4 \times 10^{-4} / 6.7 = 1.25 \times 10^{-4} \text{ min.}^{-1}$$

Similarly, at 204.5°,

$$K_{eq.} = 5.6 \text{ liters/mole}$$

$$k_5 = k_4/K_{eq.} = 2.2 \times 10^{-3} / 5.6$$

$$k_5 = 3.9 \times 10^{-4} \text{ min.}^{-1}$$



The general form of the Arrhenius equation, expressing the relation of the reaction velocity and temperature is

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad (31)$$

in which  $k$  is the reaction rate constant,  $E$  is a constant termed the energy of activation,  $R$  is the molar gas constant, and  $T$  is the absolute temperature. Integrating this equation between the limits of  $T_2$  and  $T_1$ ,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \cdot \frac{T_2 - T_1}{T_2 T_1} \quad (32)$$

where  $k_2$  is the reaction rate constant at  $T_2$  and  $k_1$  is the reaction rate constant at  $T_1$ . Using the value of  $k_{204.5}/k_{189.5}$  for each reaction, the energies of activation were calculated. The data are recorded in Table 25, page 79.

Equation (31) may be integrated without limits:

$$\ln k = -E/RT + \ln s \quad (33)$$

where  $\ln s$  is the integration constant.

$$\text{Then } k = s e^{-E/RT} \quad (34)$$

For gaseous reactions it has been shown that  $e^{-E/RT}$  is an expression of the fraction of the molecules in the reaction system having energy equal to or greater than the activation energy  $E$ (42). For bimolecular reactions  $s$  refers to the number of molecules colliding and usually has a value of about  $10^{10}$  or  $10^{11}$  when the rate constants are expressed in liters/mole-min. For unimolecular reactions  $s$  usually has a value of about  $10^{14}$  or  $10^{15} \text{ min.}^{-1}$ . Attempts have been made to associate  $s$  for these unimolecular reactions

with the frequency of vibrations in a molecule(43).

The values of  $\log s$ , calculated at  $189.5^\circ$  are given in column 3, Table 25. All of the reactions have values of  $s$  following these general rules except the decomposition of the dimer to allo-ocimene. The large error involved in the determination of the rate constants for this reaction makes the deviation in the value of  $s$  of doubtful significance. It does, however, suggest that the unimolecular decomposition of the dimer occurs through a mechanism such that the second order rate of formation of the activated complex is *not* as rapid as the unimolecular decomposition of the activated complex to form allo-ocimene.

Table 25  
Energies of Activation

<u>Reaction</u>	<u>E<sub>Act.</sub>(cals.)</u>	<u>log s</u>
Racemization of $\alpha$ -pinene	44,150	15.8
$\alpha$ -pinene $\longrightarrow$ dipentene	39,850	14.6
$\alpha$ -pinene $\longrightarrow$ allo-ocimene	42,000	15.3
2(allo-ocimene) $\longrightarrow$ dimer	28,200	10.2
dimer $\longrightarrow$ 2(allo-ocimene)	31,200	10.8

Summary.- From the data presented in this chapter the over-all reaction appears to be:

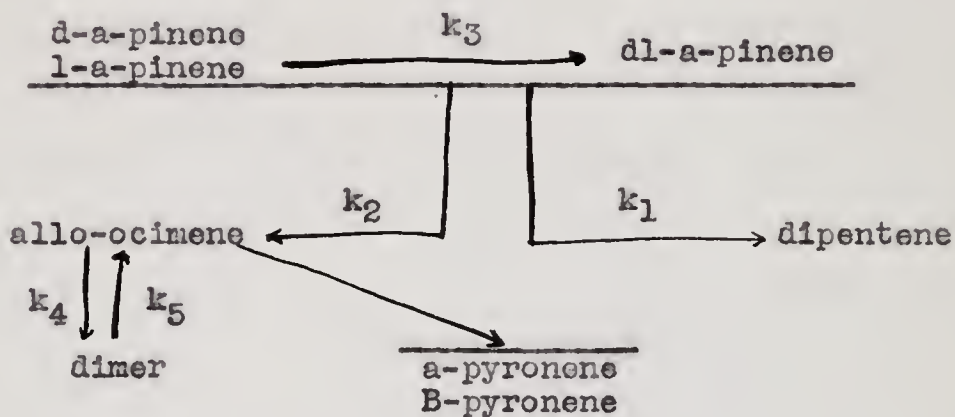


Table 26

Summary

	Rate Constant $\times 10^5$ (189.5°)	Rate Constant $\times 10^5$ (204.5°)	Energy of Activation	$\log s$
$k_1$ (min. <sup>-1</sup> )	6.13	23.9	39,850	14.6
$k_2$ (min. <sup>-1</sup> )	2.86	12.0	42,000	15.3
$k_3$ (min. <sup>-1</sup> )	0.93	4.2	44,150	15.8
$k_4$ (liters/ mole-min.)	84	220	28,200	10.2
$k_5$ (min. <sup>-1</sup> )	12.5	39	31,200	10.8



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## Appendix

Table 27

## Plate Determination

Column No.	Refractive Index of Sample in Head	Refractive Index of Sample in Kettle	Number of Plates
1	1.4005	1.4130	22
2	1.3970	1.4110	24
3	1.4045	1.4154	21
7	1.3888	1.4164	70
8	1.3910	1.4196	64

Table 28

## Determinations of Operating Holdup

Column No.	Weight Text Mixture, g.	Initial % Stearic Acid	Final % Stearic Acid	Operating Holdup, ml.
1	24.7	10.2	17.5	11.4
2	19.7	9.75	21.0	12.1
3	35.0	10.7	17.6	15.3
8	23.8	10.5	15.9	9.1

Table 29

Fractionation of Commercial  
 $\alpha$ -Pinene in Column 7

Fraction No.	Volume Fraction ml.	$n_D^{25}$
1	84	1.4628
2	66	1.4630
3-17	1550	1.4631
18-38	1495	1.4632
39	75	1.4638
40	47	1.4671
41	75	1.4762
42	60	1.4767
43-44	80	1.4768



Table 30

Fractionation of a Mixture of  
 $\alpha$ -Pinene, Camphene and B-Pinene in Column 7

Fraction No.	Volume Fraction ml.	$n_D^{25}$
1	3	1.4605
2	65	1.4630
3-13	197	1.4631
14	30	1.4632
15	25	1.4633
16	15	1.4636
17	15	1.4639
18	25	1.4641
19	8	1.4649
20	18	1.4657
21	30	1.4679
22	20	melts above 25°
23-25	120	melts 46-48° solidifies 45-44°
26	10	melts above 25°
27	30	1.4721
28	15	1.4741
29	15	1.4754
30	15	1.4757
31-34	78	1.4768

Table 31

Fractionation of a Mixture of  
Carbon Tetrachloride and Cyclohexane in Column 8

$\text{CCl}_4$ :  $n_D^{25}$  1.4561

Cyclohexane:  $n_D^{25}$  1.4230

Fraction No.	Volume ml.	$n_D^{25}$	B.P. (762 mm.) °C.
1	2.0	1.4492	77.1
2	2.0	1.4496	77.1
3	3.0	1.4531	77.1
4	2.0	1.4530	77.1
5	2.0	1.4521	77.1
6	2.0	1.4527	77.1
7-8	4.1	1.4517-1.4519	77.1
9-13	10.0	1.4522-1.4528	77.1
14	2.0	1.4521	77.1
15	2.0	1.4516	77.1
16	2.1	1.4509	77.1
17	1.6	1.4499	77.1
18	1.0	1.4482	77.1-77.3
19	1.0	1.4476	77.4
20	0.8	1.4478	77.4-77.8
21	1.2	1.4435	77.8-78.0
22	0.8	1.4421	78.0-78.1
23	1.1	1.4388	78.1-78.5
24	0.9	1.4350	78.5-79.0
25	1.0	1.4322	79.0-79.4
26	0.4	1.4298	79.4-80.0
27	1.7	1.4272	80.0-80.5
28	1.4	1.4252	80.5-80.7
29	1.2	1.4244	80.7-80.8
30	0.8	1.4240	80.8
31-32	5.0	1.4232	80.8
33-35	7.1	1.4230	80.8
36	3.0	1.4229	80.8
37-40	7.4	1.4228	80.8
41	2.4	1.4243	Residue

Table 32

Fractionation of a Mixture of  
a-Pinene and B-Pinene in Column 8

Fraction No.	Volume Fraction ml.	$n_D^{25}$
1	1.0	1.4632
2-5	7.0	1.4631
6	1.5	1.4632
7-9	3.5	1.4633
10	1.3	1.4637
11-12	2.8	1.4633
13	1.0	1.4650
14	0.5	1.4708
15	0.7	1.4735
16	0.5	1.4757
17	0.9	1.4762
18	0.3	1.4766
19	0.4	1.4766
20-26	12.3	1.4767

Table 33

Distillation of a Mixture of  
 $\alpha$ -Pinene and Commercial Dipentene in Column 8

Fraction No.	Volume ml.	29 n <sub>D</sub>	B.P. (20 mm.) °C.
1	2.0	1.4612	53.0-53.5
2-3	4.1	1.4617	53.5
4	2.0	1.4616	53.5
5-7	6.0	1.4617	53.5
8-11	8.0	1.4618	53.5-53.3
12	2.0	1.4617	53.3
13	2.0	1.4618	53.3
14-17	8.0	1.4617	53.3
18	2.0	1.4617	53.3-55
19	2.0	1.4491	55-66
20	1.0	1.4592	66-68.5
21	1.5	1.4677	68.5-?
22	1.4	1.4719	69.2-70.0
23-26	8.2	1.4732	69.5-70.3
27	2.0	1.4731	70.0-70.5
28	2.0	1.4729	70.5
29-30	4.0	1.4728	70.0
31	2.0	1.4726	70.0
32	2.0	1.4726	71.0
33	2.0	1.4725	71.0
34	2.0	1.4721	71.0
35	2.0	1.4719	71.0



Table 34

## Fractionation of Terpene Alcohols in Column 8

Fraction No.	Volume Fraction	<sup>25</sup> n <sub>D</sub>	B.P. (20 mm.) °C.
1	2.0	1.4606	106-106.5
2	2.0	1.4608	106.5-107
3	2.2	1.4608	107
4-5	6.2	1.4610	107
6	2.0	1.4612	107
7	4.0	1.4603	107-108
8	15.0	1.4610	108-110
9	1.8	1.4632	110-116
10	1.0	1.4643	116-118
11	1.8	1.4650	118
12	1.7	1.4653	118
13	2.7	1.4660	118-122
14	1.4	1.4660	122-123.5
15	0.6	1.4713	123.5-126
16	1.0	1.4701	126
17	0.7	1.4803	126-126.5
18	0.8	1.4802	126.5
19	0.9	1.4888	126.5-127
20	0.8	1.4902	127-128
21	1.4	1.4923	128
22	4.0	1.4928	128
23	2.7	1.4926	128-129
24	1.6	1.4931	129-129.5
25	about 0.5	1.4928	Residue

Table 35

Analysis of Tube No. 1  
(Heated at 189.5°C. for 20.5 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-4	35.6	51.5	1.4631	48.80	48.80			
5-8	23.7	51.6	1.4632	32.45	32.00	0.45		
9	3.2	51.6	1.4633	4.38	4.26	0.12		
10	2.4	----	1.4640	3.29	2.87	0.42		
11	0.7	----	1.4671	0.96	0.42	0.54		
12	1.1	----	1.4732	1.51		1.45	0.06	
13	1.1	----	1.4710	1.51		1.49	0.02	
14	1.3	----	1.4761	1.78		1.63	0.15	
15	1.0	----	1.4805	1.37		1.17	0.20	
16	0.4	----	1.4870	0.55		0.42	0.13	
17	0.4	----	1.5140	0.55		0.21	0.34	
Corr.	0.5		1.5415	0.66			0.66	
18	1.6	polymer	1.5140	2.19				2.19
Totals	73.0				88.4	7.9	1.6	2.2

Table 36

Analysis of Tube No. 2  
(Heated at 189.5°C. for 20.5 hours)

Fract. No.	Wt. Fr. gms.	B.P. (18 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1	9.8	50.5	1.4633	12.50	12.14	0.36		
2-4	48.2	50.5	1.4631	61.50	61.50			
5-6	9.3	50.5	1.4632	11.87	11.70	0.17		
7	1.6	----	1.4635	2.04	1.92	0.12		
8	1.6	53-						
		68.8	1.4668	2.04	0.98	1.06		
9-10	3.6	69.0	1.4703	4.60		4.60		
11	1.0	70-						
		85	1.4868	1.28		0.99	0.29	
12	1.8	85	1.5359	2.30		0.18	2.12	
Corr.	0.5		1.5415	0.62			0.62	
13	1.0	pol.	1.5130	1.28				1.28
Totals	78.4				88.3	7.5	3.0	1.3

Table 37

Analysis of Tube No. 3  
(Heated at 189.5°C. for 51 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1-4	41.5	52.9	1.4631	53.70	53.70			
5	11.7	53.0	1.4632	15.14	14.92	0.22		
6	4.8	53.4	1.4634	6.21	5.95	0.26		
7	2.1	54-						
		72	1.4651	2.72	1.96	0.76		
8-10	10.4	72.0	1.4702	13.45		13.45		
11	1.5	72-						
		87	1.4918	1.94		1.64	0.30	
12	2.5	87-						
		88.2	1.5386	3.23		0.13	3.10	
Corr.	0.5		1.5415	0.65			0.65	
13	2.3	pol.	1.5169	2.97				2.97
Totals	77.3				76.5	16.4	4.1	3.0

Table 38

Analysis of Tube No. 4  
(Heated at 189.5°C for 51 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1-4	43.7	52.9	1.4631	56.70	56.70			
5	9.5	52.9	1.4632	12.34	12.16	0.18		
6	4.9	53.5	1.4634	6.37	6.10	0.27		
7	1.4	54-						
		72	1.4651	1.82	1.31	0.51		
8	3.7	72.0	1.4701	4.81		4.81		
9	3.7	72.0	1.4703	4.81		4.81		
10	4.1	72-						
		77	1.4706	5.33		5.31	0.02	
11	1.0	77-						
		87	1.5220	1.30		0.35	0.95	
12	2.5	88	1.5410	3.25		0.02	3.23	
Corr.	0.5		1.5415	0.65			0.65	
13	2.0	pol.	1.5162	2.60				2.60
Totals	77.0				76.3	16.2	4.9	2.6

Table 39

Analysis of Tube No. 5  
(Heated at 189.5°C. for 82 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1	7.7	51.6	1.4630	10.97	10.97			
2-3	16.3	51.6	1.4631	23.20	23.20			
4-6	15.5	51.8	1.4632	22.10	21.79	0.31		
7-8	4.0	51.9	1.4633	5.71	5.55	0.16		
9	1.4	----	1.4638	2.00	1.80	0.20		
10	1.6	52.5						
		-56	1.4647	2.28	1.77	0.51		
11	0.2	----	1.4649	0.28	0.21	0.07		
12	0.2	----	1.4689	0.28	0.05	0.23		
13	2.7	66-						
		69	1.4695	3.85	0.38	3.47		
14-17	9.2	69.3	1.4702	13.10		13.10		
18	2.8	----	1.4713	4.00		3.94	0.06	
19	0.3	----	1.4758	0.43		0.40	0.03	
20	1.9	----	1.5106	2.71		1.17	1.54	
21-22	1.9	87	1.5400	2.71		0.05	2.66	
Corr.	0.5		1.5415	0.71			0.71	
23	4.0	pol.	1.5130	5.71				5.71
Totals	70.2				65.7	23.6	5.0	5.7

Table 40

Analysis of Tube No. 6  
(Heated at 189.5°C. for 82 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-3	13.5	51.4	1.4631	18.80	18.80			
4-8	26.1	51.6	1.4632	36.40	35.88	0.52		
9	1.4	52.0	1.4634	1.95	1.87	0.08		
10	2.7	52.6	1.4637	3.76	3.44	0.32		
11	1.8	53.5	1.4642	2.50	2.11	0.39		
12	0.2	----	1.4647	0.28	0.22	0.06		
13	1.9	54	1.4650	2.65	1.94	0.71		
14-17	12.4	70-						
		70.1	1.4702	17.27		17.27		
18	1.8	----	1.4708	2.50		2.48	0.02	
19	1.1	----	1.4920	1.53		1.06	0.47	
20	1.3	----	1.4888	1.81		1.34	0.47	
21	1.6	86	1.5365	2.23		0.15	2.08	
22	1.3	----	1.5387	1.81		0.07	1.74	
Corr.	0.5		1.5415	0.69			0.69	
23	4.2	pol.	1.5170	5.85				5.85
Totals	71.8				64.2	24.5	5.5	5.8



Table 41

Analysis of Tube No. 40  
(Heated at 189.5°C. for 130 hours)

Fract. No.	Wt. Fr. (gms.)	B.P. (20.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	4.8	52.5-52.8	1.4635	6.29	6.29			
2	5.7	52.9	1.4629	7.46	7.46			
3-6	26.4	53.0	1.4631	34.58	34.58			
7	3.1	53-71	1.4663	4.06	2.23	1.83		
8-9	23.8	72.0	1.4702	31.20		31.20		
10	1.4	72-88	1.4980	1.83		1.11	0.72	
11	3.5	88.0	1.5403	4.48		0.06	4.42	
Corr.	0.5			0.65			0.65	
12	7.2	pol.	1.5207	9.43				9.43
Totals	76.4				50.5	34.2	5.8	9.4

Table 42

Analysis of Tube No. 41  
(Heated at 189.5°C. for 130 hours)

Fract. No.	Wt. Fr. (gms.)	B.P. (20.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	7.0	52.5-52.8	1.4636	9.20	9.20			
2	9.1	52.9	1.4630	11.95	11.95			
3	17.8	53.0	1.4631	23.40	23.40			
4	3.6	53.0	1.4632	4.73	4.66	0.07		
5	2.4	53-71.5	1.4680	3.16	0.98	2.18		
6	2.2	71.5-71.9	1.4701	2.89		2.89		
7-9	22.2	71.9	1.4703	29.20		29.20		
10	4.3	87-88	1.5380	5.65		0.25	5.40	
Corr.	0.5		1.5415	0.66			0.66	
11	7.0	pol.	1.5200	9.20				9.20
Totals	76.1				50.2	34.6	6.1	9.2

Table 43

Analysis of Tube No. 7  
(Heated at 189.5°C. for 178 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	n <sub>D</sub> <sup>25</sup>	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	4.0	52.5	1.4637	5.24	4.80	0.44		
2	5.3	52.8	1.4638	6.94	6.25	0.69		
3-4	18.7	52.8	1.4640	24.50	21.40	3.10		
5	4.9	54.0	1.4644	6.42	5.25	1.17		
6	1.8	58-						
		71	1.4702	2.36		2.36		
7-8	24.7	71.5	1.4710	32.40		32.08	0.32	
9	2.5	71.5	1.4711	3.28		3.25	0.03	
10	1.2	72-						
		86.5	1.4964	1.57		0.99	0.58	
11	3.4	86-9	1.5334	4.45		0.49	3.96	
Corr.	0.5		1.5415	0.66			0.66	
12	9.3	pol.	1.5208	12.18				12.18
Totals	76.3				37.7	44.5	5.6	12.2

Table 44

Analysis of Tube No. 8  
(Heated at 189.5°C. for 178 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	n <sub>D</sub> <sup>25</sup>	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	2.8	52.4	1.4637	3.67	3.36	0.31		
2	4.1	52.7	1.4636	5.37	4.99	0.38		
3	6.4	52.7	1.4639	8.38	7.43	0.95		
4-5	12.1	52.7	1.4640	15.85	13.85	2.00		
6	6.0	----	1.4643	7.86	6.53	1.33		
7	1.3	54-62	1.4668	1.70	0.81	0.89		
8	0.3	----	1.4655	0.39	0.26	0.13		
9	1.4	62-71	1.4708	1.84		1.82	0.02	
10-11	28.0	71.5	1.4710	36.70		36.29	0.41	
12	4.5	86-89	1.5340	5.90		0.60	5.30	
Corr.	0.5		1.5415	0.66			0.66	
13	8.9	pol.	1.5197	11.67				11.67
Totals	76.3				37.2	44.7	6.4	11.7

Table 45

Analysis of Tube No. 9  
(Heated at 189.5°C. for 250.5 hours)

Fract. No.	Wt. Fr. gms.	B.P. (18 mm.)	$n_{D}^{25}$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1	6.1	50.6	1.4632	8.25	8.14	0.11		
2	4.8	50.6	1.4631	6.50	6.50			
3	2.8	50.6	1.4632	3.79	3.74	0.05		
4	3.2	51.0	1.4634	4.33	4.15	0.18		
5	4.3	51-64	1.4667	5.82	2.92	2.90		
6	1.9	64-67	1.4690	2.57	0.43	2.14		
7-12	32.9	68	1.4702	44.50		44.50		
13	0.9	----	1.4886	1.22		0.91	0.31	
14	4.0	85-86	1.5355	5.42		0.44	4.98	
Corr.	0.5		1.5415	0.68			0.68	
15	12.5	pol.	1.5191	16.92				16.92
Totals	73.9				25.9	51.2	6.0	16.9

Table 46

Analysis of Tube No. 10  
(Heated at 189.5°C. for 250.5 hours)

Fract. No.	Wt. Fr. gms.	B.P. (18 mm.)	$n_{D}^{25}$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1	7.5	50.5	1.4633	10.50	10.20	0.30		
2	4.8	50.6	1.4634	6.72	6.44	0.28		
3-4	5.0	51.0	1.4637	7.00	6.41	0.59		
5	3.8	51-67	1.4670	5.32	2.39	2.93		
6	1.6	67-68	1.4689	2.24	0.41	1.83		
7-11	28.3	68.0	1.4703	39.70		39.70		
12	1.2	68.0	1.4715	1.68		1.65	0.03	
13	1.3	68.0	1.4706	1.82		1.81	0.01	
14	1.3	68.0	1.4706	1.82		1.81	0.01	
15	4.0	85-86	1.5347	5.61		0.53	5.08	
Corr.	0.5		1.5415	0.70			0.70	
16	12.1	pol.	1.5191	16.95				16.95
Totals	71.4				25.8	51.4	5.8	17.0



Table 47

Analysis of Tube No. 11  
(Heated at 189.5°C for 377 hours)

Fract. No.	Wt. Fr. gms.	B.P. (18.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1-3	8.2	51.0	1.4633	11.12	10.80	0.32		
4	1.7	51-52	1.4636	2.30	2.14	0.16		
5	1.1	54-63	1.4661	1.49	0.86	0.63		
6	0.9	63-69	1.4695	1.22	0.12	1.10		
7-15	41.4	70.0	1.4702	56.10		56.10		
16	1.0	70-84	1.4821	1.35		1.12	0.23	
17	1.6	84-85	1.5270	2.17		0.43	1.74	
18	1.9	---	1.5412	2.57			2.57	
Corr.	0.5		1.5415	0.68			0.68	
19	15.5	pol.	1.5187	21.00				21.00
Totals	73.8				13.9	59.9	5.2	21.0

Table 48

Analysis of Tube No. 12  
(Heated at 189.5°C. for 377 hours)

Fract. No.	Wt. Fr. gms.	B.P. (18.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	8.3	51.0	1.4634	10.82	10.36	0.46		
2	3.0	51-53	1.4644	3.91	3.20	0.71		
3	0.7	53-58	1.4668	0.91	0.44	0.47		
4	1.4	63-68	1.4700	1.83		1.83		
5-11	43.0	70.0	1.4702	56.10		56.10		
12	0.9	70-85	1.5183	1.17		0.38	0.79	
13	2.8	86-87	1.5393	3.65		0.11	3.54	
Corr.	0.5		1.5415	0.65			0.65	
14	16.1	pol.	1.5187	21.00				21.00
Totals	76.7				14.0	60.0	5.0	21.0



Table 49

Analysis of Tube No. 13  
(Heated at 189.5°C. for 607 hours)

Fract. No.	Wt. Fr. gms.	B.P. (21 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	1.0	53.0-						
		53.4	1.4637	1.31	1.11	0.20		
2	1.8	53.4-						
		55	1.4639	2.36	2.09	0.27		
3	1.8	55-67	1.4680	2.36	0.73	1.63		
4	2.5	67-						
		72.5	1.4706	3.29		3.27	0.02	
5	1.9	72.5-						
		73	1.4705	2.50		2.49	0.01	
6-9	43.0	73.0	1.4702	56.50		56.50		
10	1.3	73-78	1.4748	1.71		1.60	0.11	
11	2.7	87-90	1.5338	3.55		0.38	3.17	
Corr.	0.5		1.5415	0.66			0.66	
12	19.6	pol.	1.5180	25.78				25.78
Totals	76.1				3.9	66.3	3.9	25.8

Table 50

Analysis of Tube No. 14  
(Heated at 189.5°C. for 607 hours)

Fract. No.	Wt. Fr. gms.	B.P. (21 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	1.2	52.8-						
		53.0	1.4628	1.57	1.57			
2	1.6	53.0-						
		53.2	1.4632	2.09	2.06	0.03		
3	1.0	53.2-						
		56	1.4648	1.31	1.00	0.31		
4	1.0	56-61	1.4682	1.31	0.36	0.95		
5	1.0	61-70	1.4727	1.31		1.31		
6	1.2	70-						
		71.8	1.4710	1.57		1.57		
7	1.3	71.8-						
		72.8	1.4705	1.70		1.70		
8	4.6	72.8	1.4704	6.01		6.01		
9-14	40.3	72.8	1.4702	52.70		52.70		
15	0.9	73-88	1.4783	1.18		1.04	0.14	
16	1.5	89-90	1.5352	1.96		0.17	1.79	
17	0.9	90-91	1.5402	1.18		0.02	1.16	
Corr.	0.5		1.5415	0.65			0.65	
18	19.5	pol.	1.5182	25.50				25.50
Totals	76.5				5.0	65.8	3.7	25.5

Table 51

Analysis of Tube No. 15  
(Heated at 204.5°C. for 7.33 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19.5 mm.)	$n_{25}^D$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1-5	58.8	51.9	1.4631	83.20	83.20			
6	3.4	52-						
		70.8	1.4668	4.81	2.30	2.51		
7	4.6	70.8	1.4703	6.51		6.51		
8	1.5	71-85	1.5140	2.12		0.81	1.31	
9	1.5	85-88	1.5378	2.12		0.11	2.01	
Corr.	0.5		1.5415	0.71			0.71	
10	0.4	pol.	1.5247	0.57				0.57
Totals	70.7				85.5	9.9	4.0	0.6

Table 52

Analysis of Tube No. 16  
(Heated at 204.5°C. for 7.33 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19.5 mm.)	$n_{25}^D$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1-3	38.1	51.8	1.4631	49.35	49.35			
4-6	27.3	51.9	1.4632	35.40	34.90	0.50		
7	2.0	52-69	1.4660	2.59	1.53	1.06		
8	6.0	69-71	1.4698	7.77	0.44	7.33		
9	1.9	71-87	1.5410	2.46		0.02	2.44	
10	0.8	87	1.5400	1.04		0.02	1.02	
Corr.	0.5		1.5415	0.65			0.65	
11	0.6		1.5230	0.78				0.78
Totals	77.2				86.2	8.9	4.1	0.8

Table 53

Analysis of Tube No. 17  
(Heated at 204.5°C. for 13.75 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-2	26.4	52.2	1.4631	34.50	34.50			
3	14.8	52.3	1.4633	19.35	18.81	0.54		
4-5	15.6	52.3	1.4632	20.40	20.11	0.29		
6	1.6	52.3-71	1.4677	2.09	0.73	1.36		
7	9.9	71.0	1.4702	12.95		12.95		
8	1.5	71.0	1.4709	1.96		1.94	0.02	
9	5.0	71-88	1.5344	6.54		0.65	5.89	
Corr.	0.5		1.5415	0.65			0.65	
10	1.2		1.5193	1.57				1.57
Totals	76.5				74.1	17.7	6.6	1.6

Table 54

Analysis of Tube No. 18  
(Heated at 204.5°C. for 13.75 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-5	55.1	52.1	1.4631	70.55	70.55			
6	2.5	52.1	1.4632	3.20	3.15	0.05		
7	4.2	52.1-71.0	1.4692	5.38	0.75	4.63		
8	10.2	71-72	1.4738	13.07		12.41	0.66	
9	4.4	72-88	1.4509	5.64		0.06	5.58	
Corr.	0.5		1.5415	0.64			0.64	
10	1.2		1.5189	1.54				1.54
Totals	78.1				74.4	17.2	6.9	1.5

Table 55

Analysis of Tube No. 19  
(Heated at 204.5° C. for 20 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	n <sup>25</sup> <sub>D</sub>	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-2	28.8	52.2	1.4631	38.40	38.40			
3	13.2	52.3	1.4632	17.62	17.37	0.25		
4	4.6	52.3	1.4633	6.13	5.95	0.18		
5	5.0	52.3-72	1.4669	6.67	3.10	3.57		
6	13.5	72.0	1.4702	18.00		18.00		
7	2.8	72-86	1.5049	3.74		1.92	1.82	
8	4.0	86-88	1.5411	5.33			5.33	
Corr.	0.5		1.5415	0.67			0.67	
9	2.6	pol.	1.5192	3.47				3.47
Totals	75.0				64.8	23.9	7.8	3.5

Table 56

Analysis of Tube No. 20  
(Heated at 204.5° C. for 20 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	n <sup>25</sup> <sub>D</sub>	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-2	33.6	52.2	1.4631	45.60	45.60			
3	14.5	52.2-60	1.4638	19.68	17.74	1.94		
4	3.0	60-72	1.4668	4.07	1.95	2.12		
5-6	13.7	72.0	1.4702	18.62		18.62		
7	2.7	72-85	1.5201	3.67		1.10	2.57	
8	3.3	85-88	1.5400	4.48		0.09	4.39	
Corr.	0.5		1.5415	0.68			0.68	
9	2.4	pol.	1.5188	3.26				3.26
Totals	73.7				65.3	23.8	7.6	3.3



Table 57

Analysis of Tube No. 21  
(Heated at 204.5° for 25 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1-3	41.9	52.4	1.4631	55.40	55.40			
4	7.2	52.4-72	1.4677	9.52	3.35	6.17		
5	15.9	72.0	1.4702	21.00		21.00		
6	1.0	72-86	1.5019	1.32		0.73	0.59	
7	5.4	86-89	1.5402	7.14		0.14	7.00	
Corr.	0.5		1.5415	0.66			0.66	
8	3.8	pol.	1.5195	5.02				5.02
Totals	75.7				58.7	28.0	8.3	5.0

Table 58

Analysis of Tube No. 22  
(Heated at 204.5°C. for 25 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% a-pinene	% di-pentene	% allo-ocimene	% polymer
1	4.2	52.3	1.4630	5.60	5.60			
2-8	36.7	52.3	1.4631	48.95	48.95			
9	2.5	52.3-53	1.4634	3.33	3.19	0.14		
10	2.8	53-72	1.4690	3.73	0.63	3.10		
11-12	13.3	72.0	1.4702	17.74		17.74		
13	4.2	72-73	1.4714	5.60		5.51	0.09	
14	1.5	73-85	1.4874	2.00		1.52	0.48	
15	2.1	85-88	1.5342	2.80		0.29	2.51	
16	3.5	88-89	1.5416	4.67			4.67	
Corr.	0.5		1.5415	0.67			0.67	
17	3.7	pol.	1.5193	4.93				4.93
Totals	75.0				58.4	28.3	8.4	4.9

Table 59  
Analysis of Tube No. 23  
(Heated at 204.5° for 34 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19.5 mm.)	$n_{25}^D$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	3.0	51.8	1.4632	4.12	4.06	0.06		
2-4	29.9	51.8	1.4631	41.00	41.00			
5	4.0	52-70	1.4662	5.48	3.08	2.40		
6	4.2	70-						
		70.9	1.4702	5.76		5.76		
7	5.4	71.0	1.4709	7.40		7.33	0.07	
8	8.8	70.8	1.4703	12.03		12.03		
9	5.6	71-85	1.4730	7.68		7.37	0.31	
10	5.6	85-88	1.5391	7.68		0.26	7.42	
Corr.	0.5		1.5415	0.69			0.69	
11	6.0	pol.	1.5208	8.22				8.22
Totals	73.0				48.1	35.2	8.5	8.2

Table 60  
Analysis of Tube No. 24  
(Heated at 204.5°C. for 34 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1-2	19.4	51.7	1.4631	26.73	26.73			
3	10.8	51.7	1.4632	14.90	14.69	0.21		
4	4.3	51.8	1.4633	5.93	5.76	0.17		
5	2.3	52-70	1.4682	3.17	0.90	2.27		
6-7	19.3	70-						
		70.6	1.4702	26.60		26.60		
8	3.5	70.6	1.4707	4.82		4.79	0.03	
9	2.5	70.6-						
		86	1.5172	3.45		1.17	2.28	
10	4.1	86-88	1.5404	5.65		0.09	5.56	
Corr.	0.5		1.5415	0.69			0.69	
11	5.9		1.5197	8.14				8.14
Totals	72.6				48.1	35.3	8.5	8.1

Table 61

Analysis of Tube No. 25  
(Heated at 204.5°C. for 51 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	6.9	52.0	1.4636	9.12	8.46	0.64		
2-3	12.1	52.0	1.4634	16.00	15.32	0.68		
4	4.5	52.0-						
		52.8	1.4637	5.95	5.45	0.50		
5	2.5	52.8-						
		71	1.4640	3.30	2.88	0.42		
6-7	29.5	71.0	1.4702	39.00		39.00		
8	3.1	71-72	1.4715	4.10		4.03	0.07	
9	6.2	85-88	1.5332	8.19		0.95	7.24	
Corr.	0.5		1.5415	0.66			0.66	
10	10.4	pol.	1.5180	13.74				13.74
Totals	75.7				32.1	46.2	8.0	13.7

Table 62

Analysis of Tube No. 26  
(Heated at 204.5°C. for 51 hours)

Fract. No.	Wt. Fr. gms.	B.P. (19.5 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	5.6	51.9	1.4635	7.68	7.25	0.43		
2	7.9	51.9	1.4632	10.83	10.68	0.15		
3	9.8	51.9-						
		52.3	1.4636	13.44	12.49	0.95		
4	4.3	52.3-71						
		71	1.4682	5.90	1.66	4.24		
5	13.6	71.0	1.4703	18.66		18.66		
6	15.5	71.0	1.4708	21.25		21.10	0.15	
7	2.6	71-85	1.5285	3.57		0.65	2.92	
8	3.4	85-88	1.5409	4.66		0.04	4.62	
Corr.	0.5		1.5415	0.69			0.69	
9	9.7	pol.	1.5192	13.30				13.30
Totals	72.9				32.1	46.2	8.4	13.3

Table 63

Analysis of Tube No. 27  
(Heated at 204.5°C. for 101 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% a- pinene	% di- pentene	% allo- ocimene	% polymer
1	6.1	52.4	1.4631	8.27	8.27			
2	4.3	52.4- 72	1.4666	5.83	2.85	2.98		
3-6	41.0	72.0	1.4702	55.51		55.51		
7	2.9	72-87	1.5111	3.93	1.67	2.88	2.26	
8	2.9	87-90	1.5410	3.93	0.04	0.84	3.89	
Corr.	0.5		1.5415	0.68			0.68	
9	16.1	pol.	1.5196	21.80				21.80
Totals	73.8				11.1	60.2	6.9	21.8

Table 64

Analysis of Tube No. 28  
(Heated at 204.5°C. for 101 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{25}^D$	% Total Wt.	% a- pinene	% di- pentene	% allo- ocimene	% polymer
1	6.7	52.3	1.4631	8.94	8.94			
2	4.4	52.3- 72	1.4674	5.87	2.32	3.55		
3-6	40.1	72.0	1.4702	53.50		53.50		
7	2.7	72-86	1.4851	3.60		2.85	0.75	
8	4.1	86-89	1.5406	5.47		0.07	5.40	
Corr.	0.5		1.5415	0.67			0.67	
9	16.5	pol.	1.5195	22.00				22.00
Totals	75.0				11.2	60.0	6.8	22.00



Table 65

Analysis of Tube No. 29  
(Heated at 204.5°C. for 267 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	1.1	53-60	1.4708	1.45	---	(1.45)		
2	3.0	60-72	1.4698	3.96	---	(3.96)		
3-4	30.8	72.0	1.4702	40.65		40.65		
5	9.4	72.0	1.4708	12.40		12.30	0.10	
6	4.5	72-73	1.4723	5.94		5.76	0.18	
7	2.6	73-86	1.4808	3.43		2.92	0.51	
8	2.9	86-90	1.5345	3.83		0.37	3.46	
Corr.	0.5		1.5415	0.66			0.66	
9	21.0	pol.	1.5175	27.70				27.70
Totals	75.8					67.4	4.9	27.7

Table 66

Analysis of Tube No. 30  
(Heated at 204.5°C for 267 hours)

Fract. No.	Wt. Fr. gms.	B.P. (20 mm.)	$n_{D}^{25}$	% Total Wt.	% $\alpha$ -pinene	% di-pentene	% allo-ocimene	% polymer
1	1.8	53-57	1.4680	2.40	---	(2.40)		
2	1.0	57-72	1.4720	1.33	---	(1.33)		
3-5	39.5	72.0	1.4702	52.55		52.55		
6	7.4	72.0	1.4704	9.85		9.85		
7	1.8	72-87	1.5180	2.40		0.78	1.62	
8	2.3	87-90	1.5330	3.06		0.36	2.70	
Corr.	0.5		1.5415	0.66			0.66	
9	20.9	pol.	1.5170	27.80				27.80
Totals	75.2					67.2	5.0	27.8

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## Biography

Robert Eugene Fuguitt was born on July 17, 1917, in Boone Grove, Indiana. He graduated from the public schools of Clearwater, Florida. After three years of study at the St. Petersburg (Florida) Junior College he transferred to the University of Florida. He received the Bachelor of Science degree in June, 1937, the Bachelor of Arts degree in August, 1938, and the Master of Science degree in May, 1940.

Mr. Fuguitt received a Graduate Assistantship in Chemistry at the University of Florida in September, 1937. He retained this position during the regular college sessions until January, 1940, when he transferred to the position of Research Assistant in Naval Stores.

Mr. Fuguitt is a member of the American Chemical Society, the Honor Society of Phi Kappa Phi and Gamma Sigma Epsilon Chemical Fraternity.

## Committee Report

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Date May 24, 1943

J. M. Simpson  
Dean

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